2110. LEWIS, W. K., GILLILAND, E. R., AND REED, W. A. Reaction of Methane With Copper Oxide in a Fluidized Bed. Ind. Eng. Chem., vol. 41, 1949, pp. 1227–1237; Chem. Abs., vol. 43, 1949, p. 7199.

Reaction between CH_4 and CuO deposited on silica gel, when stoichiometrically controlled to give a molal O_2:C ratio of 1.0 or slightly greater, is an effective means of producing CO and H_2 in a molal ratio of about 1:2. Reaction rates are high enough so that there is no reason for temperatures to be far in excess of those required by equilibrium. In a fluidization unit with a 4-ft. bed at 1,640° F. and 1 atm., 94% CH_4 decomposition was obtained with a selectivity of 92%. Higher conversions could be obtained with a higher temperature or a greater bed depth. The data were correlated on the assumption that the limiting factor is the reaction of CO_2 and water vapor with CH_4. The CH_4–CuO reaction occurs in 2 steps: An initial step that results in the rapid reduction of Cu and the simultaneous complete oxidation of part of the CH_4 and a 2d step that is rate-controlling and consists of the reforming of the remaining CH_4 with CO_2 and H_2O produced by the 1st step to form CO and H_2. The rates of the reforming reactions over Cu on silica gel are controlled by chemical reaction and not by gaseous diffusion.

2111. LEYE, A. R. [Gasification With Steam and Oxygen. Method for Calculating Results and Extent of Re-forming.] Gas- u. Wasserfach, vol. 83, 1940, pp. 669–672, 688–691; Chem. Abs., vol. 35, 1941, p. 3062.

Method has been developed for calculating the volumetric composition of a generator or re-formed gas, based on the knowledge of the fuel composition and the gasification mediums, such as steam or air, with the help of dimensionless factors for the fuel, gasification mediums, etc. Formulas are set up that permit calculation of the water-gas composition and requirements for fuel, gasification mediums, and efficiency. The effect of changes in fuel or gasification mediums, and other variables can be followed, and one can secure a picture of the effect of all factors on the gasification or reforming results. Examples are given for coke water gas, continuous gasification with steam and O_2 and the re-forming of CH_4 and hydrogenation gas, as well as the production of gas for synthetic purposes. Calculated values agree with those found in practice.

2112. LI, C. H. [Decomposition of Carbon Monoxide on Nickel.] Rev. Phys. Chem. Japan, vol. 2, 1929, p. 11; vol. 4, 1931, p. 118; vol. 5, 1932, p. 41; Jour. Soc. Chem. Ind. (Japan), vol. 43, 1940, B, p. 177.

Decomposition of CO on Ni takes place according to the active points of Ni in the following 3 steps: $2\,CO+3\,Ni=Ni_3C+CO_2$; $2\,CO+Ni=NiC+CO_2$; $2\,CO=C+CO_2$. Reaction (1) takes place on the most active points of the catalyst and the C of the CO is unreversibly held as Ni_3C in the Ni atom so that the Ni is poisoned. Reaction (2) occurs on the surface with the next-strongest activity on which the CO is adsorbed as NiC, which is reversibly again decomposed into C and Ni. Reaction (3) is the simple catalytic decomposition of CO on the least-active centers.

2113. LIANDER, H. Utilization of Natural Gases for the Ammonia Process. Trans. Faraday Soc., vol. 25, 1929, pp. 462–472; Chem. Abs., vol. 23, 1929, p. 4779.

Possible reactions of CH_4 with O_2, H_2O, and CO_2 were calculated from the Nernst heat theorem. Experiments were made by heating CH_4 and O_2, with and without Ni catalysts, to 550°–850°. With no catalyst the products are CO_2 and H_2O; with catalyst H_2, CO, and CO_2. Conclusion: Natural gas, air, and steam passed over a suitable catalyst at 1,000° would yield gas that could be used as a source of H_2 and N_2 for NH_3 synthesis.

LIANG, S. C. *See* abs. 3337, 3338.

LIBERMAN, A. L. *See* abs. 1706.

LILLE, R. *See* abs. 1058.

2114. LINDE, R. [Progress in Large-Scale Production of Oxygen.] Glückauf, vol. 72, 1936, pp. 114–118; Chem. Abs., vol. 30, 1936, p. 6142.

Methods of fractionating liquid air for O_2 are discussed. The Fränkl method employing intermittent regenerators in heat exchange, instead of countercurrent exchanges, has proved most efficient. 98% O_2 can now be produced at 1.5 pf. per m.^{3}

LINGH, A. E. *See* abs. 3668.

2115. LINZ, B. F. Plans for Huge Synthetic Plants Fantastic. Oil Gas Jour., vol. 46, No. 40, 1948, p. 38.

B. K. Brown, in a recent appearance before a congressional subcommittee, declared that Government proposals for the initiation of a construction program to supply 2,000,000 bbl. of synthetic oil per day has no justification either from the standpoint of military security or the cost in money, men, and steel. The costs have not yet been determined, but a study is expected to be made by fuel experts from industry and Government. The coal industry would need to be revolutionized to produce the required 468,000,000 tons or more than ⅔ of our highest annual production; to provide 2,000,000 bbl. of oil per day. To produce even 500,000 bbl. per day from natural gas would require the consumption of ½ the gas produced in 1946. To erect the required plants to produce the proposed quantity of oil would require huge amounts of steel—34 tons per ton of oil from shale per day, 49 tons from natural gas, and 70 tons from coal, not including the steel for the production of the raw material—whereas it takes only 26 tons to produce a ton of oil from petroleum at a new refinery in a new field. Furthermore, it is known that gas or coal can be used more economically as such than converted into oil. It is his conviction that more oil can be produced quicker by making steel available to the petroleum industry than by any other method and that the production of liquid fuels from crude petroleum should be given the preference. He appears to be in favor of developing synthetic fuel production, but less painfully and more soundly over a period of years, rather than by forced development.

2116. ———. Synthetic Fuels Program. Oil Gas Jour., vol. 46, No. 44, 1948, pp. 38–39.

In a hearing before a House Armed Services Subcommittee, it was brought out by E. V. Murphree, Standard Oil Development Co., that the cost of producing 2,000,000 bbl. per day of synthetic fuel by Secretary Krug's plan would be 17 billion dollars instead of 9 billion, and that it would be much cheaper either to allow the industry to develop synthetic fuels as rapidly as economic factors dictate or to stockpile petroleum oil at the rate of 500,000 bbl. per day over a period of 5 yrs. Taking oil products at $4.20 per bbl. and tankage at $1.30, the cost of the 5-yr. program would be 5 billion dollars. Discussing the question of costs, it requires for production, transportation, refining, and delivery of Gulf coast oil to New York, 5.7 ton of steel per bbl. of products per day for maximum distillate yield from crude oil and 7.8 tons for maximum gasoline yield. Comparable figures for natural gas products delivered at New York are 7.1 and 7.9 tons respectively, for coal products consumed locally 4.6 and 5.2 tons respectively, and for oil shale products refined and consumed on the Pacific coast 5.7 and 7.4 tons respectively. The capital investment for the above would be $4,300 and $6,500 for petroleum, $7,400 and $8,200 for natural gas, $7,600 and $8,500 for coal, and $6,100 and $8,400 for shale. Allowing costs of $2.78 per bbl. for crude, $0.10 per 1,000 cu. ft. for natural gas, $3.20 per ton for coal, and $1.00 per ton for shale, 5% for amortization and 10% for return on the investment, gasoline from crude, allowing credit for byproducts, costs $0.141 per gal., as against $0.128 for gasoline from natural gas, $0.166 from coal, and $0.16 from shale. The figures are based on a gasoline with an octane-no. level to satisfy a 10:1 compression ratio engine capable of giving about 30% more miles per gal. than present engines.

2117. ———. Bureau of Mines Modified Fischer-Tropsch Plant. Oil Gas Jour., vol. 49, No. 17, 1950, pp. 42–43.

Bureau of Mines 80–100-bbl.-per-day plant for converting coal to oil by a modified Fischer-Tropsch process will be tested this fall with a view to beginning integrated operations next year. The plant will consist of 5 units, respectively for O_2 production, coal gasification, gas purification, hydrocarbon synthesis, and distillation. The gasification unit has been developed by Koppers Co.; it converts pulverized coal under pressure into synthesis gas by the aid of steam and O_2. The gasifier uses about 28 tons of coal, 24 of O_2, and 35 of superheated steam to produce some 2,000,000 cu. ft. of raw synthesis gas daily. The converter will be of the internally cooled type having a fluidized bed of granular, synthetic-NH_3 type catalyst suspended in a constantly flowing body of coolant oil. The anticipated daily production of the gas-synthesis demonstration plant will include 55–60 bbl. of 75-octane-no. gasoline, 10–12 bbl. of 80 cetane diesel oil, and approximately 12 bbl. of heavy oils and waxes suitable for cracking stock.

2118. ———. Fuels Investigation. Oil Gas Jour., vol. 49, No. 45, 1951, pp. 46–47.

Senate Interior Affairs Committee began its investigation of the present and future fuel situation last week with a discussion of all energy resources. It was believed that the reserves of coal and oil would be enough to last for many years at the present rate of consumption. It was agreed that research on synthetic liquid fuels should be vigorously prosecuted but that no commercial plants should be built until production is economically feasible. The forecast was made that when synthetic fuels come into the picture the network of oil and natural-gas pipe lines now spreading over the country will provide a ready-made transportation system for the new fuels.

LIPKA, H. *See* abs. 2479.

2119. LIPSON, H., AND PARKER, A. M. B. Structure of Martensite. Jour. Iron Steel Inst. (London), vol. 149, 1944, pp. 123–141; Chem. Abs., vol. 38, 1944, p. 1195.

Martensite may be regarded as a deformed supersaturated solid solution of C in α–Fe, formed by very rapid quenching of a solid solution of C in γ–Fe. It is very reactive, decomposing to cementite and α–Fe at temperatures below 300° and as low as 100°–200°. The structure is body-centered tetragonal. Martensite would probably behave like cementite, forming H_2 and hydrocarbons with acids and hydrocarbons only with H_2. The method of formation almost certainly precludes any possibility that it is involved in the Fischer-Tropsch reaction.

2120. LIPSON, H., AND PETCH, N. J. Crystal Structure of Cementite (Fe_3C). Jour. Iron Steel Inst. (London), vol. 142, 1940, pp. 95–106; Chem. Abs., vol. 34, 1940, p. 6501.

Specimen of fine powder (through 380-mesh) was prepared by passing CO over Fe_2O_3 at 550°. Annealing at 600° resulted in partial decomposition (into a structure, probably Fe_2C) and sharpening of the cementite lines. Intensities were measured from the unannealed specimens, and spacings from one annealed at 600° for 17 hr. The structure is an almost close-packing of Fe atoms with C atoms in the interstices. The environment of the C atoms consists of 6 Fe atoms arranged at the corners of a triangular prism. The average Fe–C distance is 2.03 Å. 2 other Fe atoms are only 2.31 Å from each C. The relation of the structure to either the ferrite or austenite structures is not very obvious.

LISTER, F. *See* abs. 2824.

2121. LITKENHOUS, E. E. Hydrogenation of Nickel Carbonyl. Ind. Eng. Chem., vol. 31, 1939, p. 1060; Chem. Abs., vol. 33, 1939, p. 7498.

In reply to abs. 456, Litkenhous supports the hypothesis that the principal reaction is $2C+2H_2O=CH_4+CO_2$.

2122. LITKENHOUS, E. E., AND MANN, C. A. Hydrogenation of Nickel Carbonyl. Ind. Eng. Chem., vol. 29, 1937, pp. 934–938; Brennstoff-Chem., vol. 18, 1937, p. 468; Chem. Abs., vol. 31, 1937, p. 6830.

According to the opinion of various investigators, $Ni(CO)_4$ is the intermediate product in the hydrogenation of CO over Ni as catalyst. In order to explain this reaction mechanism and to determine the equilibrium of the ensuing reaction, $Ni(CO)_4$ was reacted with H_2 in the ratio of 1:4. The tests were performed 25°–400° and 1–75 atm. in a Ni tube 61 cm. long. The end gas was analyzed; and, on the basis of the analysis, the equilibrium constants were determined and compared with the data in the literature; at 1 atm. $Ni(CO)_4$ is stable at about 100°, but shortly above, it decomposes completely into Ni and 4 CO. Above 200° the formation of H_2O, CH_4, and CO_2 begins. At 250°, 58–60% of the end gas consists of H_2O, which then decreases with further rise in temperature. Likewise CH_4 and CO_2 are at a maximum at about 350° with 20% of the end gas. The diagrams of 5–75 atm. are basically the same as at 1 atm. except that the stable limit of $Ni(CO)_4$ with rising pressure varies at higher temperatures. For example, at 75 atm. $Ni(CO)_4$ is stable up to about 220°. In contrast, an increase in pressure up to 75 atm. is virtually without influence above 250° on the composition; H_2O, CH_4, and CO_2 maintain almost the same ratio. A fairly large amount of C deposits in the reaction tube but disappears with rising temperature. The end products CO_2, CH_4, and H_2O obtained in the hydrogenation of $Ni(CO)_4$ are identical with those that Sabatier and Senderens found in the hydrogenation of CO. It is seen that the reaction $2C+2H_2O\rightarrow CO_2+CH_4$ gave constant values over the whole reaction range, whereas other possible reactions did not. The reaction can, naturally, first occur whenever C and H_2O have formed, which occurs at 250°. Normally free C does not react with H_2O at 250°, yet the reaction sets in in the presence of the Ni formed from the $Ni(CO)_4$.

2123. LITTLE, A. D. Research—and a Greater Gas Industry. Am. Gas. Assoc. Monthly, vol. 10, 1928, pp. 661–665, 682; Chem. Abs., vol. 23, 1929, p. 2272.

Possibilities in the use of water gas for the synthesis of gaseous, liquid, and solid hydrocarbons.

LITTLE, A. T. *See* abs. 1517.

LITVIN, M. Z. *See* abs. 1652.

LIU, C. L. *See* abs. 3753.

2124. LIVINGSTON, J. W. Report on Leuna Works Near Merseberg. CIOS Rept. XXVIII–27, 1945, 11 pp.; PB 6682.

This report describes briefly the synthesis of MeOH and higher alcohols from CO and H_2; the production of synthetic detergents from the sulfonchlorides produced by the hydrogenation of Kogasin and treatment with SO_2 and Cl_2 with ultraviolet light as catalyst; the production of C_2H_4 by dehydrogenation of C_2H_6 and its polymerization to lubricating oil; the hydrogenation of coal; and the dehydrogenation of butane to butene, which is used for alkylation with H_2SO_4 as the catalyst.

LIVSHITZ, V. D. *See* abs. 1659, 1660, 1661, 1662.

2125. Lobo, W. E. Report on Oxygen Plant Development. PB 9381, 1945, 564 pp.

Comprehensive report on the design and development by the M. W. Kellogg Co. of O_2 units for the mechanical separation of O_2 from the air. The report contains extensive technical data on the properties of air and its constitutents, and presents comprehensive functional and operative data on the process in many statistical graphs and tables.

2126. ———. Oxygen by Fractionation at Low Pressures. Chem. Inds., vol. 59, No. 1, 1946, pp. 53–56; Chem. Abs., vol. 40, 1946, p. 5888.

1st successful low-pressure unit for liquid air fractionation built by the M. W. Kellogg Co. is described. The M–7 unit produces O_2 by liquefaction and fractionation of air, operating at a maximum pressure of about 100 p. s. i. g. The unit was designed to produce 1,000 std. c. f. h. of gaseous O_2 of 99.5% purity under the extreme atmospheric conditions of 120° F. ambient and 90° F. dew point, and to deliver the O_2, dry, in cylinders at 2,200 p. s. i. g. The complete removal of the CO_2 and H_2O from the inlet air is accomplished without chemical treatment by condensation in a special reversing exchanger. A diagrammatic flow sheet of the unit shows the 4 typical operating systems: Air compression, refrigeration and air purification, fractionation, and O_2 compression. Typical performance data also are plotted.

2127. ———. Production of Oxygen for Industrial Purposes. Chem. Eng. Progress, vol. 1, 1947, pp. 21–26; Petrol Eng., vol. 18, No. 8, 1947, pp. 120, 123, 126, 128; Chem. Abs., vol. 41, 1947, p. 2213.

Basic theory of the Kellogg low-pressure O_2 process is discussed, and a description is given of the unique temperature unbalance system. It is illustrated by means of a flowsheet. Tentative costs of a plant for producing 350 tons per day of 90% O_2 should be about $5,000 per ton of product per day. The total cost of producing O_2 in a plant of this size may be as low as $3.50 per ton, including 3% of plant cost for maintenance, 1.5% for taxes and insurance, 10% for depreciation, and all utilities and labor charges. This is equivalent to about $0.15 per 1,000 cu. ft.

2128. Lobo, W. E., and Skaperdas, G. T. Air Purification in the Reversing Exchanger. Chem. Eng. Progress, vol. 1, No. 2; Trans. Am. Inst. Chem. Eng., vol. 43, 1947, pp. 69–74; Chem. Abs., vol. 41, 1947, p. 1504.

Theory, a description, and the operation of the reversing exchanger developed as a part of the Collins low-pressure O_2 producer. Also described is the so-called unbalance-flow method for temperature control by means of an internal recycle system, developed by Trumpler, as a means of heat exchange and scavenging.

2128a. LoCicero, J. C., and Johnson, R. T. Oxo Reaction of Camphene. Structure of the Aldehyde and Derivatives. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 2,094–2,097.

Camphene is found to undergo the Oxo reaction smoothly when diluted with an equal volume of benzene using dicobalt octacarbonyl as catalyst. It gives liquid aldehyde of constant boiling point in 65% yield. It undergoes the Oxo reaction without rearrangement giving an aldehyde which is structurally related to isocamphenilanaldehyde by several methods of degradation. Oxidation of the aldehyde with air or O_2 gives a simple acid m. p. 56°–57° of the same chain length.

Locquin, R. *See* abs. 1260.

2129. Loeb, W. [Assimilation of Carbon Dioxide.] Ztschr. Elektrochem., vol. 11, 1905, pp. 745–752; Jour. Chem. Soc., vol. 90, II, 1906, p. 43.

In the silent electric discharge, moist CO_2 yields CO and O_2 first, HCOOH and H_2O_2 are formed slowly as secondary products. In moist CO, the main reactions are $CO+H_2=CH_2O$ and $CO+H_2O=CO_2+H_2$. HCOOH also is formed. A moist mixture of CO_2 and H_2 gives CH_2O and HCOOH; CO and H_2 give the same products with CH_2O present in greater quantities, as also CO_2. Moist CH_2O vapor decomposes mainly into CO and H_2 with small quantities of CH_4; HCOOH and H_2O vapor behave similarly. From CH_4 and CO_2, it is almost certain that alcohol can be synthesized, and alcohol is very probably one of the intermediate products of the natural synthesis.

2130. ———. [Chemical Action of Silent Discharge.] Ztschr. Electrochem., vol. 12, 1906, pp. 282–312; Jour. Chem. Soc. vol. 90, II, 1906, p. 324.

CH_2O always is formed in small amount by the interaction of H_2 and CO, the H_2 being formed by the reaction $CO+H_2O=CO_2+H_2$. By starting with a mixture of moist CO and H_2, much larger quantities of CH_2O are obtained and also glycolaldehyde $OH.CH_2.CHO$. CH_4 is always formed from mixtures of CO and H_2. CH_4 and CO give acetaldehyde, $CO+CH_4=CH_3.CHO$, but the reduction of acetaldehyde to alcohol by combination with H_2 has not yet been realized in the silent discharge.

2131. ———. [Action of the Silent Electric Discharge on Moist Methane.] Ber. deut. chem. Gesell., vol. 41, 1908, pp. 87–90; Chem. Abs., vol. 2, 1908, p. 1122.

Moist CH_4 was subjected under ordinary pressure to the silent electric discharge and obtained gaseous products consisting of CO_2, C_nH_{2n}, CO, C_nH_{2n+2}, and about 35–45% of H_2, and a colorless, insoluble, solid compound of composition $C_9H_{12}O$. On decomposition with concentrated H_2SO_4 traces of fatty acids were detected.

2132. Loew, O. [Organic Substances in Primitive Times.] Ztschr. angew. Chem., vol. 40, 1927, pp. 1548–1549; Chem. Abs., vol. 22, 1928, p. 2361.

It would be interesting to ascertain the 1st organic compounds that existed on the earth. Moissan, working with carbides, concluded that they must have been hydrocarbons. Metal carbides were probably formed as the nebular mass cooled. In time, when temperature conditions permitted H_2O to exist, the carbides were acted upon by it and hydrocarbons formed. By lightning, the hydrocarbon vapors and liquids were ignited and the atmosphere was enriched by CO_2 as a result. Evidence in favor of this theory is found in the existence of carbides and hydrocarbons in meteorites. It is possible that from CH_4 other organic compounds were produced. The oxides of Fe and Cu may have catalyzed the oxidation of CH_4 to CH_2O (I). (I), reacting with NH_3, formed by the catalytic union of its elements, might ultimately have led to the formation of asparaginic aldehyde. This, by polymerization and condensation, might have yielded a complex, which, on reduction with H_2 and H_2S, would give a substance approximating a protein in nature. (I) also might have polymerized to sugars, although the presence of acid vapors would have tended to make the end products simple sugars. Thus organic compounds, even to the extent of relatively complex proteins, could have come into existence without the catalyzing influence of chlorophyll and light.

Löfquist, H. *See* abs. 193.

Lohmar, W. *See* abs. 1037.

Lohnes, K. *See* abs. 1936.

Löhr, O. *See* abs. 3374.

Lohrer, W. *See* abs. 1088, 1089.

2133. Lohse, H. W. Products From Carbon Oxides and Water Gas. Catalytic Chemistry, Chemical Publishing Co., New York, 1945, pp. 329–347.

Lokhvitzkaya, A. P. *See* abs. 565.

Longuet, J. *See* abs. 1059.

2134. Longuet-Escard, J. [Reaction in the Solid State at Low Temperatures, in the Presence of Water.] Bull. soc. chim. France, 1949, D, pp. 153–156; Chem. Abs., vol. 43, 1949, p. 6531.

Formation of ferrites, chromites, sulfides, silicates, and aluminates was studied between room temperature and 100° in the presence of H_2O. The reaction products were identified by X-ray, thermomagnetic, and chemical methods. Several of the products formed were similar to those found in nature, notably franklinite, chalcopyrite, and antigorites. The hydroxides of Ni, Co, Zn, and Mg crystallized in the hexagonal system, type CdI_2.

2135. ———. [Structure of Several Hydroaluminates of Nickel.] Jour. chim. phys., vol. 47, 1950, pp. 238–243; Chem. Abs., vol. 44, 1950, p. 7612.

Addition of NaOH to a mixture of nitrates or chlorides of Ni and Al rich in Ni salts resulted, after washing and drying, in the formation of a hydroaluminate of Ni. An X-ray study was made of these types of compounds. The X-ray results were consistent with a structure composed of layers of hydroxyl ions and layers of metallic ions. The role of the Al might be to stabilize this type of structure by substitution for a small number of Ni ions. Such hydroaluminates of Ni have been used in the preparation of catalysts for the Fischer-Tropsch synthesis.

———. *See* abs. 1062.

2136. Lopatin, K. I. [Practical Technical Method for Removing Carbon Dioxide From Synthesis Gas.] Jour. Appl. Chem. (U. S. S. R.), vol. 20, 1947, pp. 23–35; Chem. Abs., vol. 41, 1947, p. 7061.

Elimination of CO_2 and CO from this gas is the first step in the preparation of a N_2–H_2 mixture for synthesis of NH_3. A method utilizing absorption by water is described and the effects of various factors indicated. Purification to about 0.5% CO_2 can be attained at the expense of about 100–120 m^3 H_2O per 1,000 m^3 gas.

2137. López-Rubio, F. B., and Pacheco, J. R. [Mechanism of the Catalytic Process for the Synthesis of Hydrocarbons by the Fischer-Tropsch Process.] Ion, vol. 8, 1948, pp. 86–89; Fuel Abs., 1949, No. 2916; Chem. Abs., vol. 42, 1948, p. 5643.

In the Fischer-Tropsch hydrocarbon synthesis the most active catalysts are Fe, Co, and Ni. Of these, Fe is probably the least active, but it has the advantage of being effective over a wide range of temperatures and is characterized by production of liquid hydrocarbons with CO_2 as byproduct. Co gives a product rich in olefins. Ni tends to produce CH_4, along with liquid and solid paraffins. Previous theories have attributed the catalytic action of these metals to either (1) formation of methylene groups, with carbides of the metals acting as intermediates, and polymerization of the methylene groups; or (2) formation of higher alcohols by the oxide content of the catalyst, with subsequent dehydration to olefins. According to a new theory, carbonyls of the metals are the primary active materials. The existence of a compound $[Fe(CO)_5]_4$ including long chains of CO groups is assumed. This is reduced to 2 mol. of C_8H_{18} and a Fe carbonyl of much lower CO content. After a number of reactions, with Fe_3C, C_3O_2, FeO, and Fe_2O_3 among the intermediate products, the lower carbonyl is reconverted to Fe. Over-all reactions are: $18CO+4Fe\rightarrow[Fe_2(CO)_9]_2$; $[Fe_2(CO)_9]_2+2CO\rightarrow[Fe(CO)_5]_4$; $[Fe(CO)_5]_4+34H_2\rightarrow C_8H_{18}+15H_2O+CO_2+3CO+4Fe+H_2$. The volumes of CO and H_2 to produce 1 mol. of C_8H_{18} are $10CO+17H_2$ instead of the previously given $8CO+17H_2$, and the theoretical yield of octane is only 188.4 gm. per m^3, instead of 203.5. The presence of Fe carbides and oxides in the catalyst is consistent with this theory, but these compounds only represent stages in the regeneration of the metallic Fe. Hydrocarbon formation is by substitution of H_2 for O_2 in $(CO)_n$ chains already formed. Polymerization of methylene groups is not inconsistent with this theory. The action of alkalies added to Fe catalysts may be either (1) removal of O from CO groups to give percarbonate, H then combining with C, and the percarbonate being subsequently reduced, or (2) polymerization of CO to chains, which combine with Fe to give carbonyls.

2138. Lopmann, B. [Manufacture of Motor Fuels by the Fischer-Tropsch Process.] Oel u. Kohle, vol 40, 1944, pp. 183–190; Chem. Abs., vol. 38, 1944, p. 6514.

Rather detailed description of the operation of a plant for the manufacture of motor fuels by the Fischer-Tropsch process. The synthesis gas can be produced directly in the correct proportion of $CO:H_2$ (1:2) by passing coke-oven gas directly into the water-gas generator; the gas, together with steam, is passed through the hot coke bed used for making water gas. The generator cycle is automatically (hydraulic) controlled. The coke used should have a particle size of 40–60 mm. and 60–90 mm., and the melting point of the coke slag should be high, which is especially important when coke-oven gas is used directly in the generator because of the high temperature required for the conversion of CH_4. The operation of the generator must be carefully supervised, since otherwise much maintenance work is required. The gas flow through the generator during the different phases of the operation is shown in a diagram. The synthesis gas is passed through a conventional gas-purifying mass, which reduces the S content to 0.2–0.5 gm. H_2S and 10–20 gm. organic S compounds per 100 m^3 of gas. Further purification is effected by passing the preheater (200°–300°) gas over a catalyst, which converts the organic S into H_2S. If coke-oven gas has been fed into the generator, the gas is passed over activated C before catalytic desulfurization, since a small amount of tarry matter containing S compounds is carried even past the generator. The temperature in the catalyst chambers is controlled by the circulation of water under pressure through a tube system (600 tubes per chamber) connected with a steam boiler. Because of the low heat conductivity of the catalyst, the cooling tubes are not in contact with the catalyst directly but with the metal plates on which the catalyst rests. The temperature is kept constant within a few tenths of a degree by regulating the steam pressure in the circulating system. The synthesis products are partly directly cooled by water injection and partly recovered by adsorption on activated C. The activated C is cooled after regeneration by contact with cooled gas. The residual gas is recycled 2 or more times, and the tail gas from the last stage is particularly well suited as fuel for coke ovens. The plant is largely automatically operated. The steam produced in the course of the process is used almost entirely for the generation of electricity, and the plant can be made independent from outside energy sources.

2139. Lopmann, B., and Jaeckel, B. [Compilation of Patents Now in Force in the Field of Methanol Synthesis.] Ber. Gesell. Kohlentech., vol. 4, 1931, pp. 1–20; Chem. Abs., vol. 26, 1932, p. 1896.

Review of German patent situation on catalysts, purification of gases, processes, equipment, and working up the product.

Lord, H. D. *See* abs. 330.

2140. Lorenzen, G. [Gas Purification, Especially Desulfurization and Sulfur Recovery.] Chem. Fabrik, vol. 12, 1939, pp. 6–23; Chem. Abs., vol. 33, 1939, p. 2312.

Review of modern methods of removing dust, tar, NH_3, C_6H_6, NO, and S from gases intended for use in syntheses, with 48 cuts of apparatus and 55 refs.

2141. LORMAND, C. Industrial Production of Synthetic Methanol. Ind. Eng. Chem., vol. 17, 1925, pp. 430–432; Chem. Abs., vol. 19, 1925, p. 2027.

This paper, based on a lecture by Patart before the Société d'encouragement pour l'industrie national, reviews the development of the process for the synthesis of MeOH by catalysis under pressure. A small industrial plant is described, utilized primarily for studying the action of various catalysts. The process operates within a temperature range of 300°–600° C., at a pressure between 150–200 atm., and with a gaseous mixture of H_2: CO in the ratio of 2:1. The pressure may be increased to as much as 900 atm. without deleterious results. A catalyst of Cu and Zn appeared to be the most efficient, although the oxides of V, Cr, and Zn gave good results as did also metallic salts such as chromates, manganates, vanadates, molybdates, and tungstates. The cost of producing MeOH in a plant having a daily capacity of 7.5 ton is calculated at $0.05–$0.07 per l. or $0.18–$0.26 per gal.

2142. LOSANITSCH, S. M., AND JOVITSCHITSCH, M. Z. [Chemical Synthesis by Aid of the Dark Electric Discharge.] Ber. deut. chem. Gesell., vol. 30, 1897, pp. 135–139; Chem. Zentralb., 1897, I, p. 354; Jour. Chem. Soc., 1897, I, p. 179.

Using a current of 3–5 amp. and 70 v., a mixture of CO and H_2O yields HCOOH, while CO_2 and H_2O give HCOOH, and O_2; CO and H_2 yield CH_2O, which polymerizes; CO_2 and H_2 yield HCOOH. On subjecting mixtures of equal volumes of CH_4 and CO to the silent discharge, acetaldehyde and its condensation and polymerization products are obtained.

2143. LOTTERI, A. [Catalytic Incomplete Oxidation of Methane With Free Oxygen.] Kraftstoff, vol. 17, 1941, pp. 137–140; Brennstoff-Chem., vol. 22, 1941, p. 211; Chim. e ind. (Milan), vol. 23, 1941, pp. 126–129, 175; British Chem. Abs., 1942, B, I, p. 19; Chem. Abs., vol. 35, 1941, p. 5284.

Equilibrium constant at different temperature of the synthesis gas reactions $CH_4+\frac{1}{2}O_2=CO+2H_2+8.8$ cal. was calculated from the published equilibrium constants of the reactions (*a*) $CH_4=C+2H_2$, (*b*) $C+CO_2=2CO$, (*c*) $CH_4+H_2O=CO+3H_2$, and (*d*) $CH_4+2O_2=CO_2+2H_2O$. In mixtures of CH_4 and O_2 above 650°, incomplete combustion of CH_4 prevails over complete combustion (d) more and more with rising temperature. Calculation for a mixture comprising O_2, 33; CH_4, 66; and N_2, 1% shows that at 750°–850° the equilibrium has shifted almost entirely towards the formation of synthesis gas ($CO:H_2=1:2$). When a 2:1 mixture of 92.1% CH_4 and 97–98% O_2 was passed at different space velocities at 890°–960° through a quartz tube filled with a catalyst (ceramic carrier saturated with aqueous Ni nitrate containing activators, subsequently calcined and reduced with H_2), the experimental and calculated data were in good agreement. At 900°, only 1–2% of CH_4 remained at all space velocities employed, and at 920°–960° the residual CH_4 was <1%. Since small quantities of heavy hydrocarbons contained in the original gas mixture were completely converted at low temperature, they appear to be more readily oxidizable than CH_4. Tests made in alloy steel tubes yielded similar results; this fact together with the good performance of the catalyst, indicate that technical application of the process is possible but especially since the reaction velocity is > in the cases of conversion of CH_4 with CO_2 (*b*) or with H_2O (*c*).

2144. ———. [Synthesis of MeOH From a Mixture of CO_2+3H_2.] Chimica e industria (Milan), vol. 24, 1942, pp. 275–278; Chem. Zentralb, 1943, I, p. 209; Chem. Abs., vol. 38, 1944, p. 3411.

Calculations are given for the reaction rate over different catalysts, with CO_2 and H_2 from butyric acid fermentation.

2145. ———. [Incomplete Oxidation of Methane With Free Oxygen.] Rev. combust. liquides, vol. 1, 1947, pp. 19–29; British Abs., 1948, B, II, p. 581; Chem. Abs., vol. 42, 1948, p. 4442.

Incomplete oxidation of CH_4 with free O_2 is examined from both thermodynamical and experimental aspects. Mixtures of CO and H_2 in the ratio of 1:2 can be obtained, and can be used in the synthesis by high or low pressure processes of alcohols, hydrocarbons, and various other derivitives.

———. *See* abs. 2559.

LOVE, K. S. *See* abs. 832.

LOWDERMILK, F. R. *See* abs. 1429.

2146. LOWRY, M. [Complete Synthesis of Fats. Synthetic Butter.] Mat. grasses, vol. 29, 1945, p. 66; Ind. chim., vol. 33, 1946, p. 46.

Fischer synthesis produces variable quantities, depending upon the pressures used, of high-molecular-weight paraffins. Oxidation of these by air transforms them into fatty acids, which can be esterified by means of synthetic glycerin made from propylene. The product has received the name "synthetic butter." It is not certain that the synthetic product has the same physiological properties as natural fats. Certain constituents are lacking, and they contain acids with both odd and even numbers of C atoms, whereas natural fats contain only the even-numbered atoms.

LUDE, A. *See* abs. 1647.

2147. LUDECKE, —. [Synthetic Benzine.] Seifensieder-Ztg., vol. 55, 1928, pp. 6–8; Chem. Abs., vol. 22, 1928, p. 1458.

Summary of the status of coal hydrogenation and production of hydrocarbons from CO.

2148. LUEBKE, A. [Synthetic Production of Fat From Coal.] Süddeut. Molkerei Ztg., vol. 68, 1947, pp. 182–183; Chem. Abs., vol. 43, 1949, p. 6327.

Review of production of synthetic fats, with arguments for and against their use as food.

LUEDEKE, V. *See* abs. 2178.

2149. LUGOL, G. [Utilization of Cracking Gas and Natural Gas in Chemical Synthesis.] Ann. mines et carburants, vol. 134, 1945, pp. 401–455; Chem. Abs., vol. 40, 1946, p. 1776.

The possibilities offered by large amounts of cracking gas available through the various processes of petroleum refining are studied. The discussion extends to the utilization of natural gas. 4 general types of applications are given in form of a review: (1) Polymerization and alkylation of the olefins by either thermal or catalytic procedures, whereby known American processes are discussed; (2) synthetic rubbers; (3) general reactions, such as the production of alcohols, formation of alkyl halides, oxidation of olefins with the production of ethers, and the formation of glycols; (4) the industrial reactions of CH_4 such as the production of $CO–H_2$ mixtures for hydrocarbon synthesis, manufacture of C black, manufacture of C_2H_2, and production of H_2.

LUK'YANOVA, L. I. *See* abs. 3369.

2150. LURGI GESELLSCHAFT WÄRMETECHNIK M. B. H. Production of Synthetic Methanol. Board of Trade, German Div. Tech. Information and Documents Unit; F. D. 204/47, Nov. 18, 1946, 3 pp.; Fuel Abs., No. 2390, 1948.

Production of MeOH by catalytic reaction of CO and H_2 under high temperature and pressure and the preparation of crude gas from various raw materials are described. The Lurgi pressure gasification in combination with the Lurgi cracking plant for the cracking of CH_4 into CO and H_2 makes it possible to combine production of MeOH with that of town gas. The plant made by Lurgi and standardized for a capacity of

12–50 tons per day is claimed to have the special advantage that the heat exchanger and the vessel containing the catalyst are arranged in a single high pressure unit. Flow diagrams and operation data.

2151. LUYKEN, W., AND KRAEBER, L. [Magnetic Properties of Natural and Artificial Iron-Oxygen Compounds. I. Magnetic Measurements on Powdered Specimens.] Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf, vol. 16, 1934, pp. 169–178; Chem. Abs., vol. 29, 1935, p. 434.

Method was developed for measuring paramagnetic and ferromagnetic substances in the form of powder, and its application in the determination of magnetic properties of Fe-O compounds is described. Magnetization curves of different material.

2152. LUYTEN, L. [Kinetics of the Methane Synthesis on Nickel.] Natuurw. Tijdschr., vol. 23, 1941, pp. 25–26; Chem. Zentralb., 1942, I, p. 25; Chem. Abs., vol. 37, 1943, p. 3662.

Experiments on the poisoning effect of CO on the active Ni used as catalyst in the synthesis of CH_4 from CO and H_2, including those in which D was used, show that the reaction velocity, $S_{CH_4}=k[H_2]\frac{1}{2}/[CO]\frac{1}{2}$ and $S_{CD_4}=k^1[D_2]\frac{1}{2}/[CO]\frac{1}{2}$, where $k^1/k=1.15$ and 1.025 at 250° and 300°, respectively. The higher the CO content of the gas mixture and the smaller the activity of the catalyst, the greater the difference between the reaction velocities of the 2 isotopes becomes, since in both cases the number of active centers remaining for adsorption of H or D is smaller and the difference between the zero-point energies causes a relatively greater difference between the two isotopes. Apparent activation energies are: $E_{CH_4}=27{,}100$ cal.; $E_{CD_4}=24{,}900$ cal. $E_{\mathrm{apparent}}=E_{\mathrm{actual}}-3\lambda_{H_2}-\lambda_{CO}$, where λ is the heat of adsorption.

2153. LUYTEN, L., AND JUNGERS, J. C. [The Kinetics of the Catalytic Synthesis of Methane in Nickel.] Bull. soc. chim. Belg., vol. 54, 1945, pp. 303–318; Chem. Abs., vol. 41, 1947, p. 2310.

Reaction is characterized by a strong adsorption of CO on the catalyst and a comparatively weak adsorption of H_2 (or D). Expressions for the velocity of reaction, as derived from experimental measurements, are:

$$V_{CH_4}=k(p_{H_2})^{0.9}/(p_{CO})^{0.2},$$
$$V_{CD_4}=k'(p_{D_2})^{0.7}/(p_{CO})^{0.2}.$$

The reaction is not inhibited by the products of the reaction. The energies of activation are: $E_{CH_4}=27{,}000$ cal., $E_{CD_4}=25{,}000$ cal.

LYNCH, M. A. *See* abs. 355a.

2154. LYON, W. H., AND CRAWFORD, R. M. Methane Cracking by Partial Combustion With Oxygen or Air in Germany. U. S. Naval Tech. Mission Tech. Rept. 556–45, 1945, 15 pp.; PB 23,076.

Coke-oven gas, hydrogenation tail gas, and Fischer-Tropsch tail gas were commercially cracked by partial combustion with O_2 or air to produce raw materials for various syntheses. Feed gas consisting of N_2 and H_2 was produced for NH_3 synthesis, and various $CO–H_2$ mixtures were made for use in the MeOH, isobutanol, and Fischer-Tropsch synthesis.

2155. ———. Synthesis-Gas Purification Processes in Germany. U. S. Naval Tech. Mission Rept. (unnumbered)–45, 1945, 16 pp.; PB 40,925; Bib. Sci. Ind. Rept., vol. 3, No. 3, 1946, p. 158.

Report covers those processes that are in commercial use for the purification of large volumes of gas, such as are employed in the production of NH_3, H_2, MeOH, and synthetic oils. The topics considered are: Dusts and tar removal; I. G. alkazid process for gas purification; I. G. Claus process for recovery of S from H_2S; H_2S removal with Fe oxide; removal of organic C, CO_2, and CO; and gas purification by activated C.

LYONS, L. E. *See* abs. 1580.

LYSSAK, L. *See* abs. 2012.

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2156. MACFARLANE, A. Synthetic Fuels. Rev. Petrol. Technol., 1936, pp. 252–258.

Developments in the Fischer-Tropsch process comprehensively discussed.

2157. MACFARLANE, W. A. Synthetic Oils From Coal. The Fischer-Tropsch Process. Chem. Age, vol. 40, 1939, p. 259.

Lecture to the Manchester Literary and Philosophical Society. Work of Fuel Research Station is reviewed.

2158. MADORIO, O. [Carburizing Equilibria and the Iron-Carbon Diagram.] Tetsu-to-Hagane, vol. 24, 1938, pp. 432–439.

2159. MAIER, C. G. Reduction of Cuprous Oxide by Carbon Monoxide. Bureau of Mines Rept. of Investigations 2926, 1929, 7 pp.; Chem. Abs., vol. 23, 1929, p. 3621.

Presence of less than 0.1 mm. CO pressure in an atmosphere of otherwise pure CO_2 will act reducingly toward Cu_2O below 1,064°. The equilibrium changes with temperature in such a way that below 900° decreasing quantities of CO suffice to reduce Cu_2O. At temperatures near and above the melting point of Cu, a partial pressure of 7.6 mm. CO in otherwise pure CO_2 should reduce the dissolved CuO to 0.008%.

2160. MAILHE, A. [Synthetic Hydrocarbons.] Jour. usines gaz, vol. 48, 1924, pp. 34–37; Chem. Abs., vol. 18, 1924, p. 1464.

Modern catalytic methods may often be used advantageously to replace the older methods besides offering an explanation of the production of certain industrial hydrocarbons. The article deals, among other things, with: The hydrogenation of CO and CO_2 with Ni at 250°; preparation of saturated aliphatic hydrocarbons from alcohols by the Grignard reaction; hydrogenation of C_nH_{2n} and C_nH_{2n-2} with Ni.

———. *See* abs. 3000.

2161. MAILHE, A., AND DEGODON, F. [Catalytic Reduction by Means of Formic Acid, and the Products Obtained by Catalytic Condensation of Acetone.] Bull. soc. chim., vol. 21, 1917, pp. 61–64; Chem. Abs., vol .11, 1917, p. 3240.

HCO_2H, which, under the influence of such catalysts as Cu, Ni, and ZnO, decomposes into H_2 and CO_2, was used in the reduction of various ketones. The hydrogenation was carried out at about 300°, using Ni or Cu. The activating effect of Cu and Ni upon the dissociation was studied.

2162. MAKINO, S. [Synthesis of Higher Alcohols From Carbon Dioxide and Hydrogen at High Pressure.] Chem. Rev. (Japan), vol. 5, 1939, pp. 21–38; Chem. Abs., vol. 35, 1941, p. 7938.

Review with 35 refs.

———. *See* abs. 1882, 1883, 1884, 1885, 1888.

MAKINO, S., KOIDE, H., AND MURATA, Y. Benzine Synthesis From Carbon Monoxide and Hydrogen. LIII. Influence of Aluminum Oxide, Silver and Other Addition Agents Upon the Iron Catalyst. *See* abs. 1889.

MALAKOFF, H. L. *See* abs. 3592.

2163. Malinowski, S. [Syntheses From Carbon Monoxide.] Przemysl Chem., vol. 28, 1949, pp. 467–482.

Review of Fischer-Tropsch and related processes.

2164. Malisoff, W. and Egloff, G. Methane. Jour. Phys. Chem., vol. 22, 1918, pp. 529–575.

2165. Mampel, K. L. [Time Versus Amount of Reaction Formulas for Heterogeneous Reactions at the Phase Boundaries of Solids. I. Development of the Mathematical Methods and the Derivation of Surface Area Versus Amount of Reaction Formulas.] Ztschr. physik. Chem., vol. 187, A, 1940, pp. 43–57; Chem. Abs., vol. 35, 1941, p. 2058.

Mathematical and theoretical. The simplifying assumptions of other workers are eliminated. Mampel assumes only equal rates of nuclear formation for equal times and for equal areas of unaffected surface and a constant velocity of growth of the nuclei. The formulas apply to the induction period as well as to the principal period of the reaction. The equation of Fischbeck and Spingler for the induction period is derived.

2166. ———. [Time Versus Amount of Reaction Formulas for Heterogeneous Reactions at the Phase Boundaries of Solids. II. Time Versus Amount of Reaction Formulas for a Powder Consisting of Spherical Particles.] Ztschr. physik. Chem., vol. 187, A, 1940, pp. 235–249; Chem. Abs., vol. 35, 1941, p. 7809.

Mathematical and theoretical. Spherical particles of uniform size are assumed. For large radius the equation has the form $kt/r=1-\sqrt[3]{1-x}$, in which the symbols have their usual meaning. For small radius the equation is $x=1-c_1e^{-4k_1r^2t}$. The intermediate case is approximated by either of these equations. This intermediate type is characterized by a reaction velocity greater than that of either of the other 2 cases. For all 3 cases there is an induction period during which the reaction follows a 4th-power time law; this period is short for the first 2 cases and long for the intermediate case. The experimental testing of the results is complicated by the tendency of particles to become smaller during the course of the reaction.

2167. Manchot, W., and Manchot, W. J. [Preparation of Ruthenium Carbonyls and Nitrosyls.] Ztschr. anorg. Chem., vol. 226, 1936, pp. 385–415; Brennstoff-Chem., vol. 17, 1936, p. 232; Chem. Abs., vol. 30, 1936, p. 5139.

By reacting CO with Ru at 180° and 200 atm., an easily volatile Ru carbonyl is formed, which separates out at −80° in colorless crystals, melting at −22 to a colorless, optically sensitive liquid, which itself decomposes a little above its melting point with evolution of gas and formation of a yellowish color. After some time it crystallizes into beautiful orange flakes until finally the liquid phase completely disappears. The conversion occurs instantaneously at 50°. The formula of the volatile carbonyl is $Ru(CO)_5$, that of the orange crystals $Ru_2(CO)_9$. It is insoluble in H_2O and easily soluble in C_6H_6, alcohol, $CHCl_3$, CCl_4, and benzine; but the solutions on standing become yellow, indicating formation of $Ru_2(CO)_9$. In alkaline solution, it is a strong reducing agent. With I in C_6H_6, $RuI_2(CO)_2$ is probably formed. $Ru_2(CO)_9$ is easily produced by heating $Ru(CO)_5$ to 50°. It can be easily crystallized from C_6H_6. The crystals are quite stable to air and light, insoluble in H_2O, and soluble in organic solvents. Its solution in glacial AcH becomes lilac in direct sunlight. It is extremely stable and is believed to be due to a change in molecular size. Heated in air, $Ru_2(CO)_9$ begins to decompose at 150°. With I it forms $RuI_2(CO)_2$, orange-red. $Ru(CO)_5$ can also be prepared by heating 1 gm. RuI_3 with 5 gm. Ag in a Cu-coated autoclave with CO at 170° and 455 atm. for 24 hr. A green Ru carbonyl is formed as a byproduct in the conversion of $Ru(CO)_5$ into $Ru_2(CO)_9$. It is amorphous and insoluble in organic solvents but is soluble in pyridine and concentrated HCl. In general, it is similar to $Fe(CO)_5$ and may be the analogous Ru compound. If $Ru_2(CO)_9$ is heated in dry NO for 13 hr. at 120°, the temperature then gradually is raised to 150°, and the NO gradually is displaced by dry N_2, a red, crystalline product is obtained, $Ru(NO)_5$. It is very difficult to obtain this uncontaminated with $Ru(CO)_5$. It easily gives off NO, especially when moist. It is insoluble in H_2O, Et_2O, C_6H_6, slightly soluble in alcohol, somewhat better in acetone, and soluble in pyridine. It is reduced with H_2 at 220°; NH_3 is formed.

Manchot, W. J. *See* abs. 2167.

2168. Mando, A. [Synthetic Fuels From Lignites.] Florence, 1940, 225 pp.; Fuel Abs., March 1945, p. 236.

Direct hydrogenation of coal and the Fischer-Tropsch synthesis process are discussed. Processes for producing synthesis gas, for example, Viag, Winkler, etc., are diagrammatically described.

2168a. Manes, M. Distribution of Liquid and Solid Fischer-Tropsch Hydrocarbons by Carbon Number. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 3,148–3,151.

Equation has been derived for calculating the distribution by C number of Fischer-Tropsch hydrocarbons, based on the assumptions that chain growth in the synthesis proceeds by stepwise addition of single C atoms, and that the probability of growth, a, of a given hydrocarbon chain is independent of the C number $>C_3$, although it may vary with experimental conditions. The equation relates the distribution of the liquid and solid product to a. Its applicability to relatively crude fractionation data (gasoline, Diesel oil and wax) from a wide variety of sources indicates that the approximate constancy of a, previously observed for liquid hydrocarbons, extends to waxes, and that a is a convenient parameter for characterizing the product distribution. The eventual termination of chain growth is a necessary consequence of the equation so that selective cracking of waxes need not be postulated.

2168b. Manfredi, G. [Synthesis-Gas Manufacture From Methane and Its Uses in the Chemical Industry.] Ingegnere, vol. 24, 1950, pp. 241–246; Chem. Abs., vol. 45, 1951, p. 2,157.

Review of the use of synthesis gas in the industries of NH_3, HNO_3, NH_4NO_3, urea, MeOH, HCHO, carbon black, HCN, and C_2H_4.

2169. Mankash, E. K., Borisova, G. P., Orochko, D. I., and Frost, A. V. [Kinetics of Catalytic Cracking of Paraffin Over Activated Aluminum Silicate.] Neftyanoe Khoz., vol. 24, No. 6–7, 1946, pp. 26–34; Chem. Abs., vol. 41, 1947, p. 2879.

Cracking of wax (a Fischer-Tropsch product melting 28°–42°, mol. wt. 320) in a reaction tube packed with activated Al silicate catalyst conforms closely to equations for a unimolescular, consecutive reaction. The velocity constant decreases slightly at low feed rates. The apparent energy of activation, calculated from these equations, is 13,550 for the overall decomposition of the feed, 16,400 for the decomposition of cracked gasoline, 11,900 for the formation of gasoline, and 15,000 cal. per mol. for the decomposition of the residue recycled to the 2d pass. The difference in the values for decomposition and formation of gasoline explains why maximum yield of gasoline is lower with increase in temperature. Formulas are derived for calculating the velocity constants of catalytic cracking as a function of temperature. Calculated data on the yield of products and the optimal volumetric velocity corresponding to maximum gasoline yield are tabulated along with experimental values. They agree fairly well.

Mann, C. A. *See* abs. 2122.

2170. Mannes, L. [Byproducts of Paraffin Oxidation.] Die Chemie, vol. 57, 1944, pp. 6–11; Chem. Trade Jour., vol. 116, 1945, pp. 309, 311; Chem. Abs., vol. 38, 1944, p. 5200.

Comprehensive summary discussing raw materials, higher-molecular aliphatic acids, forerun fatty acids, aqueous and oily condensates, volatile products, hydroxy aliphatic acids, dicarboxylic acids, alcohols, aldehydes, ketones, and Na_2SO_4. 85 refs. A translation of this paper appears in BIOS Misc. Rept. 26, 1945, pp. 13–31, PB 93,709.

Mantica, E. *See* abs. 2401b, 2706c.

2171. Maquenne, L. [Action of the Oxides of Carbon on Water Vapor.] Ber. deut. chem. Gesell., vol. 16, 1883, p. 1358; Bull. soc. chim., vol. 39, Ser. 2, 1883, pp. 308–309; Jour. Chem. Soc., 1883, p. 860.

CO reacts with H_2O at 150° over Pt sponge so that after 30 hr. all the CO_2 is converted into CO and H_2. It is concluded that the system CO_2+H_2 is stable below the dissociation temperature of CO_2; and that CO is itself at low temperature a stronger reduction agent than H_2.

2172. Marcotte, E. [Liquid Fuels.] Rev. sci., vol. 62, 1924, pp. 517–522, 551–557; Chem. Abs., vol. 19, 1925, p. 2267.

Brief outline of the qualities required of liquid fuels and of the possibility of producing them by polymerization of CH_4, hydrogenation and transformation of gaseous into liquid hydrocarbons, polymerization of C_2H_2 into aromatic hydrocarbons, direct combination of CO and H_2, carbonization of coal, lignite, and peat, production of alcohol, and use of $EtOH–C_6H_6$ mixture.

Marder, M. *See* abs. 3037.

2173. Marek, L. F., and Hahn, D. A. Reactions Involved in the Synthesis of Hydrocarbons and Alcohols From Water Gas. Catalytic Oxidation of Organic Compounds in the Vapor Phase. Chemical Catalog Co., Inc., New York, 1932, chap. IV, pp. 100–135.

2174. Marek, L. F., Bogrow, A., and King, G. W. Experimental Laboratory Study on Effect of Pressure on Carbon Deposition and Rate of Reduction of Iron Oxides in the Blast-Furnace Process. Am. Inst. Min. and Met. Eng., Metals Technol., vol. 14, No. 4, Tech. Pub. 2184, 1947, 24 pp.; Chem. Abs., vol. 41, 1947, p. 4745.

Commercial hematite was sized to 8–14 mesh and reduced with mixtures of commercial compressed CO, CO_2, and N_2, simulating gas compositions occurring in various zones of an actual blast furnace. The results showed that the reduction of Fe_2O_3 proceeds by 2 steps: To FeO and reduction of FeO to Fe. Pressures of approximately 5 atm. abs. increased C deposition under the conditions used. A maximum of C deposition occurred at about 489° at 5 atm. pressure and 1 hr. exposure. The maximum deposition at the peak was more than 3 times the deposition at temperatures 50° higher or lower. The rate of ore reduction is proportional to the linear velocity at constant pressure or to the pressure at constant linear velocity.

Marelli, S. *See* abs. 8.

Mark, H. *See* abs. 355.

2175. Markley, K. S. Synthetic Fatty Acids. I. G. Farbenindustrie A.-G., Ludwigshafen, FIAT Final Rept. 362, 1945, 4 pp.; PB 1,315.

Process used for the production of synthetic fatty acids at Oppau is the same as that used by the Deutsche Fettsäure Werke at Witten (abs. 2176 and abs. 3236), except that the latter plant used only Fischer gatsch paraffins, whereas the Oppau plant used Riebeck paraffins obtained from brown-coal pitch and Tief-Temperatur Hydrierung paraffin obtained by hydrogenation of brown coal, as well as synthetic paraffins produced by the Fischer-Tropsch synthesis. A considerable amount of work had been carried out on the nutrition value and toxicity of synthetic fatty acids produced by oxidation of paraffins from all 3 sources, and various tests have indicated that synthetic fatty acid glycerides are superior to natural fats owing to the fact that they are composed very largely of saturated fatty acids. It is indicated from the results of physiological research that straight chain fatty acids, whether odd or even, are equally readily assimilated and utilized by the body at least in certain limited amounts. However, branched chain, hydroxy, keto, and dicarboxylic acids, all of which are present in the synthetic acids, are not readily assimilated, if at all, and lead to retarded growth and abnormal excretion products in the urine. However, it is possible to remove the oxygenated and dicarboxylic acids and the branched-chain acids by suitable treatment.

2176. Markley, K. S., and Goss, W. H. Märkische Seifen Industrie. BIOS Final Rept. 86, 1945, pp. 25–32, PB 18,911; PB Rept. 225.

Besides the above-named plant (raw material capacity, 40,000 tons per yr.), 3 other plants have produced synthetic fatty acids: Oppau (capacity 20,000 tons); Heydebrech (20,000 tons); and Magdeburg (12,000 tons). The raw material is gatsch produced in the Fischer-Tropsch process. Material made in coal hydrogenation plants cannot be employed because it contains aromatic compounds. About 150–200 tons of fatty acids per month was the maximum used for the production of synthetic fats and margarine. Fatty acids $C_{10}–C_{18}$ (55–60% of the total fatty acids obtained) are used for edible purposes as compared with the $C_5–C_{20}$ acids (60–65% of the total fatty acids) used for soap making. A flow sheet of the process and plant for the manufacture of fatty acids is attached. The oxidation of the gatsch by air is carried out at 110° in Al vessels with stainless steel (V2A) tops and at atmospheric pressure in the presence of 0.2% $KMnO_4$ as catalyst. The reaction is continued until the mixture contains about 33–35% fatty acids, the remaining nonoxidized material being recycled. The overall yield of fatty acids is about 80%. Synthetic fats and margarine are made from the fatty acids by esterifying with glycerin at 120°–180° in the presence of a Zn catalyst. Whereas, the fatty acids themselves have a strong, unpleasant odor, the fats made from them are much better and have very good keeping qualities. It also is claimed that synthetic fats are utilized in the body as well as natural fats and are more suitable for diabetics, the explanation being that while diabetics burn the even number of C chains present in natural fats to give acetone, the odd number chains in synthetic fats, in addition to even number chains, are burned to propionic acid and finally give CO_2 and H_2O. The cost of synthetic acids in the different plants ranged RM 70–120 per 100 kg., whereas that from natural oils during the war was RM 140. The cost, however, depends upon the price of gatsch (during the war this was RM 30 per 100 kg.), and normally synthetic acids for soap making would cost 2 times as much as natural soapmaking oils in Germany and on the world market perhaps 3 times as much.

2177. ———. Oxo G. m. b. H., Ruhrchemie A.-G. BIOS Final Rept. 86, 1945, pp. 33–37; PB 18,911. PB Rept. 225.

Oxo G. m. b. H. is owned by the Ruhrchemie A.-G., I. G. Farbenindustrie A.-G., and Henkel & Cie. Fatty alcohols are made by treating the olefin products obtained from the Fischer-Tropsch process with CO and H_2 under 200 atm. pressure and 180° in presence of a Co–Mn–Th catalyst. The main part of the alcohols obtained are sulfated to obtain nonsoapy detergents. Fatty acids can be made from the alcohols by a further oxidation process, but the process is not economical. The chief alcohols made by the Oxo process have chain lengths ranging from $C_{11}–C_{18}$. The C_{13}, C_{17}, and C_{18} alcohols were very satisfactory as regards color, and the C_{17} and C_{18} alcohols were comparatively free from odor. The cost of the olefins was stated to be 35–40 pf. per kg., and they are sold to Oxo at 45 pf. The cost of the finished alcohols was 80–90 pf.

Marschner, R. F. *See* abs. 3153, 3767, 3768.

2178. Marsh, J. L., Fremon, G. H., Glenn, R. D., Luedeke, V. D., and Porter, D. J. Coming Search for Synthetic Motor Fuels. Chem. and Met. Eng., vol. 51, No. 6, 1944, pp. 107–111.

Survey, including the Fischer-Tropsch process.

2179. Marshall, A. L. Synthetic Formaldehyde From Carbon Monoxide and Hydrogen. Mechanism of the Sensitized Photochemical Reaction. Jour. Phys. Chem., vol. 30, 1926, pp. 1634–1640; Chem. Abs., vol. 21, 1927, p. 534.

Kinetic study is continued of the photochemical reaction between H_2 and CO when sensitized by Hg vapor to light of wavelength 2536.7 Å. U. from a H_2O-cooled Hg arc. The gases were saturated with Hg at 50°, and the reaction chamber was maintained at 80°. The apparatus and method were the same as those previously described. Measurements were made of the amount of energy absorbed while the reaction was proceeding. The data for the last of a series of 10 experiments were: Volume of apparatus, 890 cc.; initial gas mixture, 510 mm. CO, 279 mm. H_2; absorption rate, 1.35 $(10)^{19}$ quanta per min.; maximum rate of reaction 2.1 mm. per min. corresponding to 3.3 $(10)^{19}$ molecules of HCHO formed, or quantum yield of 2.44. The reaction product formed was largely HCHO or a polymer. In 1 experiment, 138 cc. of a theoretical 200 cc.³ of HCHO were recovered. A study of the velocity constants calculated by various possible kinetic equations makes it apparent that the velocity depends in some way on the ½ power of the H_2 and the 1st power of the CO concentration. This would seem to mean that the velocity depends on the concentration of atomic H. The most satisfactory equation expressing the velocity is $d/dt(\mathrm{HCHO})=k(\sqrt{P_{H_2}})(P_{CO})$. The reaction between CO_2 and H_2 was reinvestigated, and it was found that reaction proceeds at a relatively slow rate.

2180. Marshall, F. C. B. Scientific Utilization of Coal and Its Importance to the Paint Industry. Jour. Oil & Colour Chemists' Assoc., vol. 29, January 1946, pp. 3–13.

Emphasizes the importance of low-temperature tar in the paint industry and advocates the introduction of the Fischer-Tropsch process and processes based on C_2H_2, CaC_2 and water gas for providing chemicals for this and the plastics and rubber industries.

2181. Martin, F. [Benzine and Oil Synthesis From Water Gas.] Petrol. Ztschr., vol. 33, No. 33, 1937, pp. 1–6; Chem. Abs., vol. 32, 1938, p. 3577.

Flowsheet, representation by models, and photographs are used to explain the synthetic production of oils from water gas.

2182. ———. [Industrial Synthesis of Benzine and Oil From Water Gas.] Mitt. Forsch.-Anstalt. Gutehoffnungshütte Oberhausen A.-G., vol. 5, 1937, pp. 159–166; Oel u. Kohle Erdoel Teer, vol. 13, 1937, pp. 691–697; Ind. Chemist, vol. 13, 1937, pp. 320–326; Glückauf, vol. 73, 1937, p. 812; British Chem. Abs., 1937, B, p. 1005.

Author discusses problems arising from the large-scale application of the Fischer-Tropsch process and describes commercial plants and the properties of the synthetic products. Nature of the problems that had to be surmounted in the conversion of the Fischer-Tropsch process to the industrial scale is considered.

2183. ———. [Industrial Synthesis of Gasoline and Oil From Water Gas.] Cong. mondial pétrole, 2me Cong., Paris, Sec. 2, Phys. Chim. Raffinage, 1937, pp. 299–307; Chem. Abs., vol. 33, 1939, p. 359.

New and efficient processes have been worked out in the production of petroleum-like hydrocarbons from a mixture of CO and H_2; they solve the problems of (1) prolongation of the life of the contact mass, (2) inexpensive construction of the reaction chamber, (3) regeneration of rare metals and metal oxides from used contact masses and (4) transformation of primary synthetic product into marketable gasoline. Synthetic gas is obtained by the use of coke or lignite briquets. After passing the 1st contact mass, the primary product contains 92% liquid products, of which 22% is gas oil, 10% solid paraffins, and 60% liquids boiling up to 200°; the proportion of olefins in the lower-boiling liquids ranges from 30–55%; the gaseous products are rich in propylene and butlyene. The liquid products are converted into marketable gasoline to the extent of 80%, and the gas oil, which has a cetane no. above 100, can be recovered separately and used to improve low-grade diesel oils from other sources. High-grade lubricants also may be produced. With the contact masses now in use no material change in the boiling curve of the primary product is possible. By increasing the CO content of the entering gas, it is possible to increase the olefin content without materially changing the ratios of the various fractions, which makes it possible to obtain by polymerization a larger proportion of hydrocarbons of high molecular weight.

2184. ———. [Development of the Synthesis of Hydrocarbons From Water Gas.] Chem. Fabrik, vol. 12, 1939, pp. 233–240; British Chem. Abs., 1939, B, p. 905; Chem. Abs., vol. 33, 1939, p. 5630.

Methods of producing the gas from various fuels are reviewed and illustrated with cuts of apparatus. The effects of temperature, pressure, contact substance and the time of contact on the nature of the synthetic products are discussed. There is a suitable process available for the production of the gas from virtually every type of fuel, and with well-purified gas the synthesis of the primary hydrocarbons is independent of the source of the gas.

2185. ———. [Synthetic Paraffins for the Preparation of Fatty Acids.] Fette u. Seifen, vol. 48, 1941, pp. 395–396; Chem. Abs., vol. 37, 1943, p. 544.

Review.

2186. ———. [Fischer-Tropsch Hydrocarbon Synthesis.] Erdöl u. Kohle, vol. 1, 1948, pp. 26–29; British Abs., 1948, B, I, p. 684.

Reviews recent published work on the production of synthesis gas and its S purification, the properties of the different catalysts, and their reaction mechanisms and products.

2187. Martin, P. T. Synthesis Gas From Coal. Min. Cong. Jour., vol. 36, No. 2, 1950, pp. 55–58; Chem. Ind., vol. 66, No. 3, 1950, pp. 365–372.

Reviews all processes that have been or are being tried in producing synthesis gas for the production of synthetic liquid fuels. The process most favored appears to be that of utilizing continuous gasification of powdered coal in suspension with O_2 and steam. With present O_2 prices, it is the opinion that synthesis gas can be produced today at about $0.15/M cu. ft. from coal at $2.00/ton.

Martin, R. *See* abs. 2461.

Martin, R. M. *See* abs. 750.

Martin, W. *See* abs. 2933.

2188. Martinenghi, G. B. [Experimental and Technical Preparation of the Higher Fatty Alcohols.] Olearia 1947, pp. 309–319; Chem. Abs., vol. 42, 1948, p. 4371.

Review on preparation and sulfonation of higher fatty alcohols. Points discussed are: Extraction from spermaceti, synthesis by hydrogenation of glycerides or fatty acids, synthesis by addition of CO to olefins from Fischer-Tropsch process and subsequent hydrogenation, and reduction of glycerides or other fatty acid esters with metallic Na. 29 refs.

Marushkin, B. K. *See* abs. 2492.

Marushkin, M. N. *See* abs. 139.

Mason, L. S. *See* abs. 49.

2189. Mathews, J. A. Review and Bibliography of the Metallic Carbides. Smithsonian Miscellaneous Collections 1090 (1898).

2190. Mathieu, K. [Measurements of Specific Magnetization and Their Use in Problems of the Metallurgy of Iron.] Arch. Eisenhüttenw., vol. 16, 1943, pp. 415–423; Chem. Abs., vol. 38, 1944, p. 708.

New magnetic pendulum balance is described by which the magnetization is determined by deflection. Several examples illustrate use of the instrument from −150° to +1,000°.

Mathieu, K. *See* abs. 2059.

Mathieu, S. *See* abs. 551, 552, 553.

2191. Matignon, C. [Physicochemical Study of Some Organic Syntheses.] Bull. soc. chim., vol. 37, 1925, pp. 825–836; Chem. Abs., vol. 20, 1926, p. 38.

It is readily possible to decide from the heats of reaction and van't Hoff's equation and the principles of equilibrium whether certain synthetic reactions, starting with simple gaseous substances, could be realized, granted a suitable catalyst, or would be entirely unattainable without the introduction of energy in some form. For example, $CO+2\ H_2=MeOH+27.2$ cal. $K=(p_1\times p_2^2)/x$, where p_1, p_2 and x are the pressures of the substances concerned in atmospheres. K can be calculated for any other temperature by the relation $\log K=-27{,}200/457\ T+3.5\log T+4.3$. Then for assumed, but possible, values for p_1, p_2, x can be calculated. If it is relatively large at the temperatures and pressures used, the reaction is possible, but if x is small, the reaction could not possibly be realized. In the above case, at 227° and $p_1=p_2=50$ atm., $x=1.8\times10^3$. At $p_1=p_2=1$, $x=1/70$. At 327°, the equilibrium is less favorable but still possible, while at 427° it would be virtually useless. Similar calculations are used to show that primary aliphatic alcohols, AcOH and $EtCO_2H$ could be made from CO and H_2 but that CH_2O could not be. From C_2H_4 and H_2 the saturated hydrocarbons could be formed, also Me_2CO and PrOH from C_2H_4, CO, and H_2. From CH_4 and H_2O, CO and H_2 might be made at a rather high temperature, but CH_4 and CO and H_2 could not give EtOH nor could CH_4 alone give C_2H_6, etc. Since in general any catalyst that assists a reaction toward equilibrium also assists the opposite reaction toward equilibrium, the search by catalysts for reactions shown by the above methods to be possible can be simplified by searching for decomposition catalysts for the final substances desired. For example, find catalysts for the decomposition of AcOH to CO and H_2, and the same catalysts will serve for the synthesis of AcOH from CO and H_2.

2192. ———. [Physicochemical Study of Some Organic Syntheses.] Chim. et ind., special No., September 1926, pp. 513–519; Chem. Abs., vol. 21, 1927, p. 731.

Discussion, a priori, of the synthesis of MeOH, of aldehydes and ketones, in general, and Me_2CO, in particular, of AcOH and of $EtCO_2H$ from CO and H_2, of EtOH, C_4H_{10}, C_6H_{14}, Me_2CO, and C_3H_7OH from C_2H_4, of the syntheses starting from CH_4 and of the synthesis of nitrogenous organic compounds by the use of NH_3.

2193. ———. [Future Position of Coals as Raw Materials of the Chemical Industry.] Chim. et ind. vol. 23, 1930, pp. 543–555; Chem. Abs., vol. 24, 1930, p. 4611.

Primary byproducts of coal carbonization and petroleum cracking (H_2, CO, CH_4, C_2H_4, etc.) are surveyed and their applications in NH_3 synthesis, hydrogenation, and the syntheses of MeOH and CH_2O are indicated. CH_4 in turn may become a starting point for C_2H_2, HCN, MeCl, etc.; C_2H_4 for EtOH; and ethylene glycol for butadiene and synthetic rubber.

2194. Matignon, C., and Seon, M. [Action of Water Vapor on Methane.] Compt. rend., vol. 195, 1932, pp. 1345–1348; Chem. Abs., vol. 27, 1933, p. 1565.

CH_4 pure or mixed with H_2, N_2, O_2, and CO yields H_2 and CO_2 when mixed with a large excess of H_2O vapor and passed slowly over the catalysts SiO_2, ZrO_2, asbestos sprinkled or impregnated with ZrO_2, ThO_2, Fe_2O_3, $Fe_2O_3+10\%\ K_2CO_3$, or Al_2O_3 at 860°, 960°, 1,000°, or 1,050°. The best results for the mixture were obtained with ZrO_2. With pure CH_4 and ZrO_2 at 1,050° the reaction was complete.

2195. Matsubara, A. Chemical Equilibrium Between Iron, Carbon, and Oxygen. Trans. Am. Inst. Min. and Met. Eng., vol. 67, 1922, pp. 3–55; Chem. Abs., vol. 15, 1921, p. 1683.

Detailed report on an extended research on (1) the equilibrium composition of the gas phase in the system CO, CO_2, and Fe (containing 2–30% O) at the temperatures 873°, 1,070° and 1,175°; (2) the equilibrium composition of the gas phase in the systems (*a*) CO, CO_2, FeO (saturated with Fe), and Fe (saturated with FeO) and (*b*) CO, CO_2, Fe_3O_4 (saturated with FeO), and FeO (saturated with Fe_3O_4) at several temperatures above 700°; (3) the equilibrium composition of the gas phase of the systems (*a*) FeO, Fe_3C, CO, and CO_2 and (*b*) Fe, Fe_3C, CO, and CO_2 in the range 700°–1,100°. The specific reactions considered are (*A*) $3\ Fe_2O_3+CO\rightleftharpoons 2\ Fe_3O_4+CO_2$; (*B*) $Fe_3O_4+CO\rightleftharpoons 3\ FeO+CO_2$; (*C*) $FeO+CO\rightleftharpoons Fe+CO_2$; (*D*) $2\ CO\rightleftharpoons C+CO_2$; (*E*) $3\ FE+2CO\rightleftharpoons Fe_3C+CO_2$; (*F*) $3\ FeO+5CO\rightleftharpoons Fe_3C+4CO_2$. Pure CO was admitted to a porcelain tube containing a sample of Fe_2O_3 heated to a definite temperature. After equilibrium was attained the gas phase was withdrawn and analyzed, and the boat containing the partly reduced Fe_2O_3 was weighed to check the amount of O remaining in the solid phase. This procedure was repeated until the O in the solid phase was reduced to about 2%. To make sure of the reversibility of the reactions concerned, an already reduced solid phase (Fe–FeO) was oxidized by successive charges of CO_2. These values agreed with those obtained by reduction with CO. The equilibrium pressures within the range 561°–1,175° for reactions (B) and (C) when each system contains amorphous C are calculated from the experimental values for the composition of the gas phase. The dissociation pressures for FeO and Fe_3O_4 are also calculated. When, by successive reductions with CO, the O in the solid phase of the systems considered above is decreased to a small quantity a new reaction begins, and the solid phase contains, besides O, some combined C. The reaction of carburization takes place according to (*E*) or (*F*). From determinations of the equilibrium constants for (*E*) and (*F*) it is concluded that the 1st period of carburizing reaction coincides with (*F*) and at a later period with (*E*); that there exist transient equilibria between the above 2, between the 1st and reaction (*C*) and between the 2d and (*D*); equilibria at lower temperature occur with a more oxidized form of the solid phase than at higher temperature even in the same carburizing reaction. The limits of temperature and pressure for carburization are determined from the experimental data. Above 1,300° the carburizing action of CO does not occur; carburized Fe is oxidized to FeO–Fe solid solution by pure CO at 1 atm. pressure. Under 1 atm. pressure, at 1,200° neither carburization nor decarburization occurs in pure CO; between 1,200° and 1,300°, C-bearing Fe is decarburized by pure CO, but O-bearing Fe may be carburized by the same gas, both reactions ending in the formation of O-bearing carboniferous Fe proper to that temperature; between 695°–1,200° a gas rich enough in CO will carburize Fe; below 695° no carburization in the ordinary sense can occur. The carburization theory is applied to the practice of casehardening, the making of malleable castings, and to the explanation of a blast-furnace diagram and the problem of quick smelting.

Matsubara, I. *See* abs. 1119, 1120.

Matsumoto, E. *See* abs. 1906a.

Matsumura, A. *See* abs. 1930.

Matsumura, S. *See* abs. 2197, 2198, 2199, 2200, 2201, 2202, 2203, 2204, 2205.

2196. Matsumura, S., Tarama, K., and Kodama, S. Benzine Synthesis and Activated Adsorption of Hydrogen, Carbon Monoxide, Carbon Dioxide and Water on Cobalt and Iron. I. II. III. Sci. Papers Inst. Phys. Chem. Research (Tokyo), vol. 37, 1940, pp. 302–322 (in German); Jour. Soc. Chem. Ind. (Japan), vol. 43, suppl., 1940, pp. 175–184; Chem. Zentralb., 1940, II, p. 2842; Chem. Abs., vol. 34, 1940, pp. 6502–6503.

Physical adsorption of H_2 on Co or Fe occurs below 60°; above this temperature activated adsorption occurs until a maximum is reached at approximately 200° (Co) or 160° (Fe). Adsorption of CO by Co or Fe, although equilibrium is approached slowly, increases rapidly above 60°, the adsorption being reversible below 110° (Co), but decreases above 60° for Fe, adsorption increasing above 190°. Chemisorption of CO by Co or Fe probably results in carbide formation, Fe requiring a higher temperature for this process. Adsorption of CO_2 by Co is considerable; physical adsorption probably occurs below 100° and activated adsorption above 100°, with a maximum at 150°. Fe adsorbs considerable CO_2 at room temperature, but this adsorption decreases to a negligible amount at 300°. Co and Fe exhibit physical adsorption of N, adsorption virtually ceasing at 100° (Co) and 250° (Fe). Subtraction of the values on the adsorption curve for N on Co or Fe from those on the curve for wet N indicates roughly that activated adsorption of H_2O on Co starts about 60° and reaches a maximum at 100° and that for Fe activated adsorption begins at 200°. In the benzine synthesis, a carbide is first formed, which reacts with adsorbed atomic H to give CH_2 groups; these CH_2 groups undergo polymerization (various degrees depending on number of groups present), then reduction, and the hydrocarbons so formed volatilize from the catalyst surface. Temperatures above 160° for the synthesis of benzine with Co catalyst are necessary so that enough quantities of activated H_2 will be adsorbed on the catalyst. A higher reaction temperature is required with Fe on account of higher temperature of formation of Fe carbide. In the benzine synthesis, Co differs in its action from Fe in that H_2O instead of CO_2 is formed because of the greater desorption velocity of H_2O from the Co.

2197. Kodama, S., Matsumura, S., and Tarama, K. Physicochemical Investigations on Coal Synthesis. IV. Velocity of Adsorbing Hydrogen by Cobalt. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, pp. 823–825; Chem. Abs., vol. 42, 1948, p. 2080.

H_2 under atmospheric pressure is brought into contact with Co at 14.5°–275°, and the velocity of adsorption of H_2 by Co is measured. When t (in min.)/x (cc. H_2 adsorbed per gm. of Co) is plotted against t for each temperature, a straight line is obtained in each case; this shows that there is a relation $t/x=t/A+1/A^2K$, which is the integrated form of $dx/dt=K(A-X)^2$, where A and K are constants characteristic of each temperature. This proves the fact that H is adsorbed in the dissociated state by two active centers of Co. Study of A and K determined for various temperatures shows that on the surface of Co there are active adsorbing centers of various degrees of activity, and at low temperature the centers of greater activity react. When the temperature is raised, such centers soon become saturated with H, and then the centers of less activity begin to exhibit a measurable velocity of adsorption. Thus, the higher the temperature the greater the adsorption by active centers of smaller activity.

2198. Kodama, S., Matsumura, S., and Ando, T. [Physicochemical Investigations on Gasoline Synthesis. V. Velocity of Adsorption of Hydrogen by a Catalyst of Cobalt and Infusorial Earth.] Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, pp. 920–924; Chem. Abs., vol. 42, 1948, p. 8439.

Mechanism of adsorption of H_2 under atmospheric pressure by Co precipitated on infusorial earth is the same as in the case of pure Co, but A, determined by the number of active adsorbing centers, is much greater for the supported catalyst. The values of K, measuring the velocity of adsorption, are small, perhaps because the activity of adsorbing centers increases and most of them are instantly saturated, so that only the adsorption of less active centers is within the scope of measurement. Variation in A with temperature shows the same tendency as in the previous case.

2199. ———. Physicochemical Investigations on Gasoline Synthesis. VI. Velocity of Adsorption of Hydrogen by Cobalt–Thoria–Infusorial Earth Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, pp. 920–924; Chem. Abs., vol. 42, 1948, p. 8440.

With a catalyst of Co, ThO_2, and infusorial earth in the ratio 100:18:150, there was no change in the mechanism of adsorption, but there was further increase in A, with adsorption taking place more rapidly and with the final amount of H_2 adsorbed being greater than in previous cases. Addition of Th not only increased the number of active adsorbing centers, but also produced centers of greater activity at lower temperature, so that it greatly decreased the temperature of activated adsorption of H_2.

2200. Kodama, S., Matsumura, S., Tarama, K., Ando, T., and Yoshimori, K. Physicochemical Research on Gasoline Synthesis. VII. Velocity of Adsorption of Hydrogen by Iron. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 254–258; Chem. Abs., vol. 43, 1949, p. 2412.

Similar experiment to that previously described (abs. 2197), in which Fe was used instead of Co, was carried out at 0°–306°. When t/x is plotted against t for each temperature one straight line for 0° and 30° was obtained, and one broken line (broken at 1 point) for temperatures above 60°, except 99.6°, for which no line or lines were obtained, leading to 1 or 2 sets of values of A and K. It is concluded that H_2 is adsorbed by Fe in the dissociated form as by Co, that the surface of Fe is not homogeneous, and adsorption at the centers of the weaker activity is observed at higher temperatures. No reason for the irregularity at 99.6° was found. Values of A above 150° were much higher than below, which shows that above 150° the number of active centers of adsorption suddenly increases.

2201. ———. Physicochemical Research on Gasoline Synthesis. VIII. Velocity of Adsorption of Hydrogen by Iron on Infusorial Earth. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 254–258; Chem. Abs., vol. 43, 1949, p. 2413.

Similar experiment was performed by using Fe hydroxide precipitated on infusorial earth and dried. The result was similar to the previous experiment except that there was a shift in temperature at which irregularity and broken lines appeared. In general, it was also noticed that infusorial earth had an effect of increasing the number of active centers and increasing the activity of those centers.

2202. ———. Physicochemical Research on Gasoline Synthesis. IX. Velocity of Adsorption of Hydrogen by a Composite Iron Catalyst. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 254–258; Chem. Abs., vol. 43, 1949, p. 2413.

Similar experiment was carried out with a catalyst containing Fe, Cu, Mn, and infusorial earth in the ratio 100:25:2:125, respectively, which was reported by Tsuneoka and others (abs. 1885) to be a good catalyst in gasoline synthesis. Results similar to the case of pure Fe were obtained, except that the t/x–t curve was irregular at 25° and 60°, and above 100° it was a broken line, showing that the adsorption of H_2 above 100° conformed to the second order reaction velocity equation. In comparison with the Fe-infusorial earth catalyst, there was no marked change in the amount of H_2 adsorbed and its change with temperature at higher temperature, but below 100° the amount of H_2 adsorbed increased. This increase is considered to be caused by Cu.

2203. ———. Physicochemical Research on Gasoline Synthesis. X. Adsorption of Carbon Monoxide on Cobalt, Cobalt–Kieselguhr, and Cobalt–Kieselguhr–Thoria Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 47, 1944, pp. 1–5; Chem. Abs., vol. 43, 1949, p. 2413.

Adsorption of CO was measured at 0°–250°. In all cases, adsorption accompanied by decomposition of CO and formation of metallic carbide took place above 110° and ordinary activated adsorption took place below 110° The addition of kieselguhr and ThO_2 greatly increased the number of centers of activity and promoted the formation of carbide.

2204. ———. Physicochemical Research on Gasoline Synthesis. XII. Adsorption of Carbon Monoxide on Iron, Iron–Kieselguhr, Iron–Kieselguhr–Copper–Manganese Catalysts. Jour. Soc. Chem. Ind. (Japan), vol. 47, 1944, pp. 1–5; Chem. Abs., vol. 43, 1949, p. 2413.

Adsorption of CO at 0°–300° was measured. In all cases, adsorption accompanied by the formation of carbide took place above 150°, and the addition of kieselguhr and Cu+Mn greatly increased the velocity of carbide formation. The effectiveness of kieselguhr as carrier and promoter in gasoline synthesis is considered to be due to the increase in the number of active centers for H_2 and CO, the increase in the amount of activated adsorption of H_2 and the velocity of carbide formation, while the effectiveness of Cu+Mn as promoter lies in the increase in the number of active centers for carbide formation. The reaction temperatures of the catalysts of the Fe series are higher than those of the Co series because the Fe catalysts form carbides at higher temperatures.

2205. Kodama, S., Matsumura, S., Yoshimori, K., Nishibayashi, Y., Kadota, N., and Iwamura, E. Physicochemical Studies on Gasoline Synthesis. XIII. XV. Influence of Potassium Carbonate and Boric Acid on the Activated Adsorption of Hydrogen and Carbon Monoxide on Iron Catalysts. Jour. Soc. Chem. Ind. (Japan), Sec. vol. 51, 1948, pp 80–100; Chem. Abs., vol. 44, 1950, p. 9136.

By adding K_2CO_3 to the catalyst containing 100 Fe+25 Cu+2 Mn+125 kieselguhr, activated adsorption of CO above 200° is increased, while that of H_2 is not, especially when 6% K_2CO_3 is added. By adding H_3BO_3 to the same catalyst, adsorption of CO is decreased and adsorption of H_2 increased at 200°. When 20% H_3BO_3 and 2% K_2CO_3 are added, adsorption of both CO and H_2 at 200° is increased. The above tendency conforms with results of gasoline synthesis with the same catalyst: Increase in the length of synthesized molecules and of the I values of the oil by adding K_2CO_3 or a decrease with H_3BO_3, and an increase in yield by the addition of both.

2206. Matthews, M. A. Oxo Synthesis. BIOS Final Rept. 747, 1945, pp. 2–4, PB 52, 880.

Brief description of plant and operation at Ruhrchemie, Holten.

2207. ———. Acetylene by the Arc; Also the Oxosynthesis at Ruhrchemie, Holten. BIOS Final Rept. 747, Sept. 1946, 4 pp.; PB 52,880.

Besides the production of C_2H_2 from CH_4 by high-temperature cracking, some details are given regarding a plant that was under construction for the production of alcohols from the C_{11}–C_{14} olefins obtained from Fischer-Tropsch Kogasin by the Oxosynthesis, that is, addition of CO and H_2 under pressure to give the aldehyde and subsequent reduction by H_2 under pressure to the alcohol. The catalyst is the normal Fischer-Tropsch catalyst of Co–ThO_2–kieselguhr. The yield of alcohols is approximately 100% by weight of the olefins present in the reaction mixture. The mixed alcohols are to be used for manufacture of detergents.

2208. Matthews, M. A., and Wood, W. L. Oxidation of Hydrocarbons to Ethylene and of Methane to Acetylene With Conversions of Acetylene to Acetone. BIOS Final Rept. 877, 1945, 7 pp.; PB 52,854.

Investigation was made by oxidizing C_2H_6, C_3H_8, C_4H_{10}, and Kogasin from the Fischer-Tropsch synthesis into C_2H_4, as well as oxiding CH_4 to C_2H_2 and manufacturing acetone from C_2H_2.

2209. ———. Production of Alcohols and Ketones From Olefins at the Treibstoffwerk, Rheinpreussen. BIOS Final Rept. 131, 1946, 12 pp., PB 18,926; Fuel Abs., vol. 3, No. 5, 1946, Abs. 2315.

Waste gases from the Fischer-Tropsch plant were used as raw material, but, owing to the great need for synthetic gasoline, expansion of this work did not receive official sanction as it appears that synthetic gasoline was more urgently needed than synthetic alcohol. The same situation arose when a proposal was made by the Treibstoffwerk to crack part of their product to gaseous olefins or to run the Fischer-Tropsch reaction with a reduced H_2 partial pressure.

Matthias, B. T. *See* abs. 1136.

Matui, A. *See* abs. 2502, 2503, 2504.

2210. Matui, A., and Yasuda, M. Oxidation of Methane Under Pressure. I. Jour. Soc. Chem. Ind. (Japan), vol. 43, suppl., 1940, pp. 453–454; Chem. Abs., vol. 35, 1941, p. 3796.

Partial oxidation of a natural gas containing 94.95% CH_4 in the presence of 30% air, was studied at 350°, the variable being gas pressure and velocity of gas flow. At 100 atm. pressure (kg. per cm.²) over Fe_2O_3 as catalyst 400 mg. CH_3OH per 100 l. gas was formed; CuO and AgO gave 360 mg. and 285 mg. CH_3OH, respectively, under the same conditions. With increase of pressure the Fe_2O_3 and CuO curves increased in slope while the AgO curve decreased. The same gas mixture yielded 30 mg. HCHO over AgO and over CuO catalysts, and 23 mg. over Fe_2O_3 under 100 atm. pressure at 350° and a gas flow of 10 l. per min. The yield of CH_3OH over AgO tended to increase, over Fe_2O_3 and CuO to decrease, with increase of velocity of gas flow, while the yield of HCHO was less-affected over these catalysts.

2211. Matushita, T., and Nagasawa, K. Mechanism of the Tempering of Steels. Jour. Iron Steel Inst. (London), vol. 10, 1927, 12 pp.; Chem. Abs., vol. 21, 1927, p. 3876.

The change in electric resistance and intensity of magnetization are determined for a quenched C steel containing 1.02% C, 0.33% Si, 0.30% Mn, 0.015% P, and 0.022% S, and it is found that during the decomposition of martensite, the electric resistance decreases and the intensity of magnetization increases, both in 2 steps below 300°. It is concluded that there are 2 kinds of martensite, α and β, of which during the heating at a normal rate, the first decomposes at 100°–170° and the second at 170°–300°. In decomposing, martensite yields free C rather than cementite, and this combines with Fe in the interval 300°–400° to form cementite. This formation of cementite is believed to explain the second contraction in the thermal expansion curve as well as the sharp increase in magnetic hardness between 300° and 400°. This also is illustrated with a W steel containing the double carbide $4Fe_3C.WC$. The authors propose the following classification of the tempered structures of quenched C steels: martensite+troostite—100°–300°; troostite—300°; troostite+sorbite—300°–400°; sorbite (osmondite)—400°; sorbite+granular pearlite—400°–550°; granular pearlite—550° to Ac_1 point. This is only valid for a normal rate of heating.

2212. Maxted, E. B. Employment of High Pressures in Chemical Industry. Jour. Soc. Chem. Ind., vol. 45, 1926, pp. 366–370T; Chem. Abs., vol. 20, 1926, p. 2712.

High pressures are used (1) to increase reaction velocity, (2) to change equilibrium conditions, (3) to influence the course of a reaction, and (4) to facilitate heat transfer. Joints should be tongue and groove with metallic or vulcanized-fiber gaskets. Pipe joints should be flanged, with the end of the pipe projecting slightly to form the actual joint. Sliding parts can only be packed by some form of leather bucket. Internal heaters may have their leads carried through vessel walls by bolts in fiber sleeves with fiber gaskets protected by steel washers under the nuts. Thermocouple leads are passed through fiber tubes in the wall and the gland, with a disk of fiber under the gland as packing; or they may have a metal disk soldered to the wire and packed in the stuffing box by fiber washers above and below the disk. Brief mention is made of the significance of high pressures in the synthesis of NH_3, CH_3OH, "synthol," H_2 from H_2O and Fe, isopropyl alcohol, and hydrogenation of naphthalene.

2213. ———. Application of Catalysis in Industry. Chem. and Ind., vol. 57, 1938, pp. 759–766.

Growth of the catalytic industry is demonstrated, and the general aspects of catalysis are discussed. In heterogeneous catalysts, the surface:mass ratio is important; promoters that are not normally catalysts increase the activity of catalysts by providing a dispersion medium that avoids the formation of large crystal growths and thus increases the effective surface. Other promoters are themselves catalysts; there is direct evidence that complex associations are formed. The promoting action of alkali is discussed, although the explanation is not yet understood. Hydrogenation catalysis is discussed at some length. Hydrogenation of CO with Co–Th catalyst is employed for the production of paraffins and of unsaturated hydrocarbons, which can be polymerized to a satisfactory lubricating oil. The reaction gas mixture of H_2 and CO is cleaned of H_2S by an Fe oxide purifier, and of organic S by an alkalized Fe contact mass at 200°–300°. Thermal stability—the temperature range must be kept within 1°—is maintained by thermal stabilizing tubes containing high-pressure H_2O at 185°–215° or oil. Coal hydrogenation using 2-stage catalysts of Sn and Mo is touched upon.

2213a. ———. Poisoning of Metallic Catalysts. Advances in Catalysis, Academic Press, Inc., New York, vol. 3, 1951, pp. 129–177.

Review covers catalysts susceptible to poisoning, principal types of catalyst poisons, form of catalyst-poisoning curves, factors, influencing toxicity and beneficial poisoning. 50 refs. listed.

2213b. Maxted, E. B., and Hassid, N. Studies in Gaseous Adsorption. III. The Thermal Activation Effect in the Adsorption of Hydrogen on Platinum and Nickel. Jour. Chem. Soc., 1932, pp. 1532–1539; Chem. Abs., vol. 26, 1932, p. 3978.

Pt and Ni were allowed to adsorb H_2 at a low temperature. They were then heated to a higher temperature in H_2. The amount of adsorption at higher temperatures was normal. After cooling to a lower temperature an abnormal adsorption is obtained. The sum of the additional values obtained stepwise is substantially the same as if the heating is all one unit. The effect per degree is greater the lower the original temperature on the scale. If the heating and cooling are in a vacuum instead of in H_2 the adsorption at the lower temperature is normal. An explanation without assumption of distinctly different adsorption types is presented.

2214. Maxwell, H. L., and Hayes, A. Free Energy and Heat of Formation of Iron Carbide for the Temperature Interval 650°–700°. Jour. Am. Chem. Soc., vol. 48, 1926, pp. 584–593; Chem. Abs., vol. 20, 1926, p. 1349.

Equilibrium constants for the reaction $3Fe(\alpha)+2CO=CO_2+Fe_3C$ were measured at 1 atm.; a flow method was used and resultant gases were analyzed. The volume % CO_2 at equilibrium was 35.7 ± 0.1 at 650°, 25.25 ± 0.05 at 700°. From data of Rhead and Wheeler for equilibrium constants of reaction $2CO=C$ (graphite)$+CO_2$, ΔF for reaction $3Fe(\alpha)+C=Fe_3C$ is 3,138 cal. at 650° and 2.281 cal. at 700°. These data give ΔH at $675°=19{,}162$ cal.

2215. Maxwell, L. R., and Brunauer, S. Thermomagnetic Investigations of Promoted Iron Oxide and Iron Catalysts. Phys. Rev., vol. 76, 1949, p. 175, abstract L7.

Curie point and specific magnetization of singly and doubly promoted catalysts were determined. Singly: $Fe_3O_4+Li_2O$, Na_2O, K_2O, Cs_2O, CaO, BaO, B_2O_3, Al_2O_3, SiO_2. Curie point virtually unchanged, but specific magnetization reduced nearly 50% upon adding 1.7% by weight of BaO. Doubly: Fe_3O_4 and $Al_2O_3+Li_2O$, Na_2O, K_2O, MgO, CaO, BaO, SiO_2. Curie point varied only slightly and was >Curie point of Fe_3O_4. Large reductions of specific magnetization were observed. Some of these, reduced in H_2 behaved like pure Fe.

2216. Maxwell, L. R., Smart, J. S., and Brunauer, S. Thermomagnetic Investigations of Promoted and Unpromoted Iron Oxide and Iron Catalysts. Jour. Chem. Phys., vol. 19, 1951, pp. 303–309.

The Curie temperature (Θ) and intensity of magnetization of certain unreduced and reduced Fe oxide catalysts have been determined. For the singly promoted unreduced systems of Fe_3O_4, containing small amounts of one of the following, Na_2O, K_2O, Cs_2O, BaO, B_2O_3, Al_2O_3, or SiO_2, Θ was found to be virtually the same as for Fe_3O_4, but large reductions in the saturation intensity of magnetization were observed. The doubly promoted unreduced systems studied contained additions to Fe_3O_4 of Al_2O_3 and one of the following in small amounts: Na_2O, K_2O, BaO, or SiO_2. Θ for these materials varied only slightly and was either equal to or less than that for Fe_3O_4. Large reductions in magnetization were found. Magnetic measurements on the reduced materials gave values of Θ the same as for pure Fe. The extent to which the promoters go into solid solution, both for the unreduced and reduced materials, is determined. Additional unreduced unpromoted Fe oxides were investigated that had variable ratios (γ) of F^{++}/Fe^{+++}. Starting at $\gamma=0.352$, magnetization was found to increase with increasing γ to a maximum at $\gamma=0.50$, agreeing with the known value for magnetite, and then to decrease to a small value for large γ. The value found for magnetization at $\gamma=0.352$ is in agreement with Néel's theory of ferrimagnetism as applied to cubic Fe_2O_3 and Fe_3O_4. Θ was found to be constant at about 583° C for γ from 0.352 to 1.276.

Mayer, K. *See* abs. 3071.

2217. Mayer, M., and Altmayer, V. [Equilibrium of Methane.] Ber. deut. chem. Gesell., vol. 40, 1907, pp. 2134–2144; Jour. Chem. Soc., vol. 92, 1907, I, p. 457.

From equilibrium data calculated on the basis of investigations of the reaction $C+2\ H_2\rightleftharpoons CH_4$ in the presence of Ni or Co at temperatures 470°–620°, doubts are expressed that Bone and Jerdan (abs. 296) could have effected the synthesis of CH_4 at 1,200°. Probably the C employed contained impurities that yielded CH_4.

2218. ———. [Synthesis of Methane With Calcium Hydride.] Ber. deut. chem. Gesell., vol. 41, 1908, pp. 3074–3080; Chem. Abs., vol. 3, 1909, p. 64.

CaH_2 forms CH_4 with CO, the maximum yield (65.6%) being at 500°. The yield decreases as the temperature rises. Other products of the reaction are C and CaC_2. With CO_2 and CaH_2, the maximum yield of CH_4 is 60.24% at 500°. Less CaC_2 is produced and traces of Ca formate and oxalate and considerable quantities of $CaCO_3$ also are formed. Soot and CaH_2 at 270° give H_2 and N_2; above 270° CH_4 also is obtained. The maximum yield is 40.68% at 500° or in a stream of H_2 19%. Some Ca_3N_2 also is produced.

2219. Mayer, M., Henseling, F., Altmayer, V., and Jacoby, J. [Gas Reactions.] Jour. Gasbeleucht., vol. 52, 1909, pp. 166–171, 194–201, 238–245, 282–286, 305–313, 326–328; Chem. Zentralb., 1909, I, p. 1853; Chem. Abs., vol. 4, 1910, p. 2724.

This work proceeds from the methods of Sabatier and Senderens for the preparation of CH_4 from H_2 and CO and from mixtures of CO_2 and H_2 with the aid of CO and Ni as catalyzers, thus: $CO+3H_2=CH_4+H_2O$; $CO_2+4H_2=CH_4+2H_2O$; $2CO=C+CO_2$. These reactions were studied in detail, the most noteworthy result of which was the synthesis of CH_4 from its elements, $C+2H_2=CH_4$; Ni, Co, and Fe were the catalyzers used. While Co brings about the union of C and H_2 almost as readily as Ni, yet with Fe only small amounts of CH_4 were obtained, which fact is explained by the oxidation of Fe by the oxides of C. As for the form of C to be used, the finely divided grade obtained by decomposition of CO afforded the most rapid reaction. From graphite, lampblack, and electrolytic C only small quantities of CH_4 were obtained. Using the same catalyzers, further investigations were made with steam in place of H_2, to which the following water-gas reactions are applicable: $CO+H_2O=CO_2+H_2$, $C+2H_2O=CO_2+2H_2$ and secondarily $CO_2+4H_2=CH_4+2H_2O$. The information so obtained was then considered in connection with illuminating gas, and possible technical applications with reference to the water gas process discussed. Since gas reactions, in general, are limited by equilibrium, and their determination is possible from equilibrium constants, the thermal relations, and the specific heats of the substances according to thermodynamic formulas, the conditions of the synthesis of CH_4 were more closely studied. Finally, it was demonstrated how, theoretically, by combining the conditions of equilibrium of CO_2 and CH_4 the quantitative relations of the equation $CO_2+CH_4\rightleftharpoons 2CO+2H_2$ are developed. If this last equation is combined with the expression of equilibrium $CO_2+H_2\rightleftharpoons CO+H_2O$, the equations for the synthesis of CH_4 result: $CO+3H_2\rightleftharpoons CH_4+H_2O$ and $CO_2+4H\rightleftharpoons CH_4+2H_2O$.

2220. Mayland, B. J., and Hays, G. E. Thermodynamic Study of Synthesis-Gas Production From Methane. Chem. Eng. Progress, vol. 45, 1949, pp. 452–458; Chem. Abs., vol. 43, 1949, p. 7200.

General thermodynamic equations for synthesis-gas production from natural gas are presented. From these a chart was prepared for determining an equilibrium mixture, outside the C deposition boundary, at pressures 1–21.4 atm., temperatures 1,200°–2,500° F. and H_2:CO ratios 1.75–2.25. This chart is particularly applicable to calculations related to the steam-CO_2 reforming process wherein, maximum yield, based on the natural gas, is obtained at maximum conversion, and consumption of steam and CO_2 depends on the excess required to prevent C deposition at equilibrium. This assumes that only CO and H_2 are formed with no C, C_2H_2, or C_2H_4. The maximum yield and the minimum consumption of CO_2 and steam are favored by high temperatures and pressures. The equilibrium calculations for the adiabatic reaction of CH_4 and O_2 and of CH_4 and air to give synthesis gas are presented also. In order to obtain final equilibrium temperatures in the range of 2,350° F., which are necessary to attain equilibrium without the use of a catalyst, a considerable excess of O_2 is required. Maximum yield of synthesis gas, based on natural gas or O_2 consumption, are obtained at some temperatures below 2,200° F. depending upon the pressure used. Therefore, a catalyst is necessary for maximum yields in the partial oxidation process.

2221. Mayor, Y. [Manufacture of Formaldehyde.] Rev. chim. ind. (Paris), vol. 46, 1937, pp. 34–40, 70–77, 110, 111–116, 136–140; Chem. Abs., vol. 31, 1937, p. 6191.

General description and discussion of the various methods of manufacture of CH_2O (dehydrogenation or oxidation of MeOH, partial oxidation of hydrocarbons, hydrogenation processes), with a description of the various forms in which CH_2O is marketed and their preparation. 147 refs.

2222. ———. [Manufacture of Methanol and Formaldehyde by Oxidation of Methene.] Ind. chim. belge, vol. 26, 1939, pp. 291–292; Chem. Abs., vol. 34. 1940, p. 4053.

Review with 13 refs.

2223. ———. [Synthetic Fats.] Rev. sci., vol. 78, 1940, p. 149; Chem. Zentralb., 1940, II, p. 569.

Short description of preparation of higher fatty acids from paraffin.

2224. ———. [Synthetic Gas. Its Application in the Chemical and Fuel Industries.] Chaleur et ind., vol. 26, 1945, pp. 63–70; Ind. chim., vol. 32, 1945, p. 252.

Review of actual and possible uses of synthetic gas and the modern methods of production. Special mention is made of the water gas process by means of external heating developed by G. Szigeth and adopted in the German Didier process and the French Cie. générale de construction de fours and known as the Syngaz process. It produces a gas suitable for the Fischer synthesis with a ratio of $CO:H_2::1:2$. A French company is actually constructing a plant of this type in the south of France using the Fuveau lignites as raw material. The gas will be used for producing MeOH and for producing fuel by the hydrogenation of raw materials of that region, such as heavy petroleum oils, shale and lignite oils, etc.

2225. Mazza, F. P. [Synthetic Petroleum and Benzine.] Saggiatiore, vol. 3, 1942, pp. 9–12; Chem. Zentralb., 1942, II, p. 2964.

Brief review of the petroleum industry, cracking and pressure hydrogenation of hydrocarbons, tars, coal liquefaction, CO hydrogenation, and the processes involving the products, such as oxidation to fatty acids, lubricants from the polymerization of olefins, isobutyl alcohol, and synthetic rubber from cracking gases.

McAteer, J. H. *See* abs. 2325a.

2226. McCance, A. Balanced Reactions in Steel Manufacture. Trans. Faraday Soc., vol. 21, 1925, pp. 176–201; Jour. Soc. Chem. Ind., 1926, B, p. 364.

Equilibrium constants of several reactions in steel manufacture have been derived theoretically, and the equations for Fe and Fe oxides have been evaluated.

McCartney, J. T. *See* abs. 54.

2227. McCartney, J. T., and Anderson, R. B. Crystalline Aggregation of Cobalt Powder. Jour. Appl. Phys., vol. 18, 1947, pp. 902–903; Chem. Abs., vol. 42, 1948, p. 805.

In electron-microscopic studies of Fischer-Tropsch catalysts, an interesting phenomenon was observed in Co metal powder reduced from cobaltous oxide. The oxide particles sintered into larger smooth droplets of Co that were aggregated into thin, hexagonal platelets. X-ray diffraction analysis showed the presence of the hexagonal crystal phase of Co. A possible explanation is that the aggregates are formed by forces similar to those operating in normal crystal formation, but of reduced magnitude insufficient to destroy the identity of the component particles. It is not evident why this phenomenon has been observed only in Co.

2227a. ———. Electron Microscopic Replica Studies of Porosity in Fused-Iron Catalyst. Jour. Appl. Phys., vol. 22, 1951, pp. 1441–1443; Chem. Abs., vol. 46, 1952, p. 4339.

Preparation of various replicas of a fused-Fe (Fe_3O_4–MgO–K_2O) synthetic NH_3 catalyst is described. Micrographs of these replicas show comparable fine structures that are attributed to the pores developed in the catalyst upon reduction. Dimensions of these fine structures compare reasonably well with pore diameters calculated from pore volume-surface area determination.

2228. McCartney, J. T., Seligman, B., Hall, W. K., and Anderson, R. B. Electron Microscopic Study of Metal Oxides and Metal Oxide Catalysts. Jour. Phys. and Colloid Chem., vol. 54, 1950, pp. 505–519; Chem. Abs., vol. 44, 1950, p. 5691.

Changes in structure of Fe_2O_3 gel, hydrous NiO, CuO powder, Ag_2O powder, CoO powder, Co basic carbonate, Co–ThO_2–MgO (100:6:12) catalyst, Co–kieselguhr (100:200) catalyst, Co–ThO_2–MgO–kieselguhr (100:6:12:200) catalyst, and Fe_2O_3 catalyst (Fe:Cu:K_2CO_3, 100:10:0.5) on reduction were studied by determination of weight losses and comparisons of electron micrographs and surface areas by N_2 adsorption. Surface areas determined from particle sizes from micrographs and by adsorption permit estimating porosity. The individual differences in structure and changes on reduction are described. Precipitated oxides and catalysts always showed decrease in surface area on reduction, and a sizable portion of this decrease occurred in reduction rather than by sintering. Decrease in sintering on reduction of Co basic carbonate is effected by the addition of promoters and kieselguhr, the order of increasing effectiveness being kieselguhr$<ThO_2$, MgO$<ThO_2+$MgO. Electron micrographs are useful but difficult to interpret unless combined with the surface-area determinations by gas adsorption.

McDonald, H. J. *See* abs. 3158.

McGee, J. P. *See* abs. 768, 3100.

McKeever, C. H. *See* abs. 3670.

2229. McKinney, A. R. Decomposition of Ethylene and Carbon Monoxide on Metallic Catalysts. Jour. Phys. Chem., vol. 47, 1943, pp. 152–163; Chem. Abs., vol. 37, 1943, p. 3659.

Metals Fe, Co, and Ni rapidly decompose CO above 250°, whereas Os, Pt, Cu, and Pd are comparatively inactive. The active group of metals all form carbonyls. The order of decreasing activity for C_2H_4 decomposition by Ni, Co, Fe, and Cu is compared to their respective atomic radii, 1.24, 1.25, 1.27, and 1.28 Å. Ni and Co decompose C_2H_4 increasingly to CH_4 as the temperature is raised; the C_2H_6 formation goes through a maximum at about 280°. Cu produces no CH_4 up to 460°, the reaction products being H_2 and C_2H_6. With Fe large amounts of both H_2 and CH_4 are formed. From an equimolecular C_2H_4–CO mixture the decomposition of C_2H_4 reaches 90% at 10°–60° lower temperature than without CO. The relative yields of H_2, C_2H_6, and CH_4 are considerably influenced by the CO. Evidence as to the source of catalytic activity is reviewed.

2230. McMillan, W. G., and Teller, E. Assumptions of the Brunauer, Emmett, and Teller Theory. Jour. Phys. and Colloid Chem., vol. 55, 1951, pp. 17–21. Chem. Abs., vol. 45, 1951, p. 3220.

An adsorption-isotherm equation valid in the region of multilayer adsorption is obtained, which takes into account both the effect of surface tension of the adsorbate and the effect of the extension of the adsorbent attractive forces beyond the 1st adsorbed layer. The differences between this derived equation and one of identical functional form obtained earlier are usually negligible numerically.

2231. Medsforth, S. Promotion of Catalytic Reactions. I. Action of H_2 on CO and CO_2. Jour. Chem. Soc., vol. 123, 1923, pp. 1452–1469; Chem. Abs., vol. 17, 1923, p. 3271.

CO was 99.8% pure. The H_2 was electrolytic and 99.9% pure. CO_2 was used directly from cylinders. The catalyst, Ni, was deposited from purified salts on purified pumice in the proportions 0.1 gm. of reduced Ni to 1 gm. of pumice. The reactions involved were $CO+3H_2=CH_4+H_2O$ and $CO_2+4H_2=CH_4+2H_2O$. To provide an excess of H_2, the proportions used were H_2:CO::5:1 and H_2:CO_2::6:1, by volume. The maximum catalytic effect was measured by the maximum speed at which the mixed gas could be passed over the catalyst and promoter with almost complete removal of the CO or CO_2. The reaction chamber was a straight tube fused to a preheating coil that surrounded it. The several promoters associated with 0.1 gm. of Ni on 1 gm. of pumice in the order of decreasing efficiency in accelerating the speed of the gaseous reactions are as follows: Ce, Th, Be, Cr, Al, Si, Zr, Mo, and V oxides (Sn and Mg oxides and Cu and Ag produce no acceleration). The formation of CH_4 from H_2 and CO or CO_2 probably consists in the formation of intermediate addition products of the MeOH type followed by the splitting off of H_2O. The CH_2 resulting is immediately hydrogenated to CH_4. Or a complex intermediate product, H_4NiCOH_2, forms and decomposes into Ni, CH_4, and H_2O. In either case, Ni must caatlyze by acting as both a hydrogenating agent and as a dehydrating agent. It is not a good agent for the latter process. The substances that promote its catalytic action are good dehydrating agents. When CH_3OH+3H_2 is passed over Ni the decomposition into CO and H_2 is much more rapid that the formation of CH_4 and H_2O. If thoria is added, the rate of formation of CH_4 is increased 14-fold. When Fe catalyzes the interaction of CO and H_2O to form CO_2 and H_2 the most effective promoters are O carriers and hydrating agents. This indicates that H_2 is produced through the formation of formic acid as well as by alternate oxidation and reduction. The oxidation of a gas in a gas mantle may be considered to consist of the addition of O_2 to form an intermediate compound and its subsequent dehydration. The catalyst should be a powerful O carrier and a strong dehydrating agent. The promoter acts (1) by decomposing intermediate compounds formed by the catalyst, or (2) by causing substances to combine, or (3) by adsorption to increase concentration. Promoters may act selectively.

2232. Medvedev, S. S. [Catalytic Oxidation of Methane to Formaldehyde. I.] Trans. Karpov Chem. Inst., No. 3, 1924, pp. 54–65; Chem. Abs., vol. 21, 1927, p. 2457.

Medvedev experimented with Au, Pt, Mn_2O_3, NiO, Al_2O_3, CuO, Ag_2O, PbO, and CeO_2 catalysts on an asbestos base. At low rates of flow (1 l. in 20 min.) and at low temperatures (250°–350°) only CO_2 is obtained. Mn_2O_3 proved to be the most, CuO the least active catalyst. At temperatures above 500° and a rate of 1 l. per min., traces of HCHO and a little CO appear besides CO_2 with CuO as a catalyst, but not with the others. This Medvedev interprets as evidence of the acceleration of all reactions by the catalysts or their nonspecificity. Glass at 600° gives a large yield of HCHO, which is attributed to the lesser chemical activity of such a surface in not being able to form peroxides as in the case of metals and their oxides. With CH_4 (containing 3–7% H_2) Pb catalysts (borates, phosphates, and their mixtures) gave the highest yields of HCHO at 500°–700°. The activity of these catalysts, however, was referred to the presence of volatile impurities, as lead chloride, since a long series of experiments showed that small concentrations of HCl (0.13%) in the gases was very beneficial in raising the relative yield of HCHO. Medvedev's best results are exceptionally high. Thus at 600° from a mixture containing 13.8% CH_4 and 17.98% O_2 with a velocity of 0.23 l. per min., the yield of HCHO was 5.02% of the CH_4 taken, 8.65% CH_4 being decomposed, that is, 58.04% of the decomposed CH_4 decomposed to HCHO.

Mehl, R. F. *See* abs. 3648, 3649.

2233. Meisenheimer, K. [Experiments With the Fischer Synthesis at Normal Pressure.] FIAT Reel R–20, frames 7,546–7,551, Oct. 21, 1938; PB 73,564.

Experiments at the Ammonia Laboratory, Oppau, deal with the influence of certain processes on the manufacture of Co catalysts and the effect of other additional catalyst metals. It was found that washing out of the Co carbonate precipitated on the carrier must be thoroughly done. Addition of Mn oxide to the Co catalyst leads to a more constant yield of paraffin after a longer reaction time. Of the rare metals La oxide and Th oxide proved to be the best additions tested. As substitutes for diatomaceous earth, kaolin and some brands of Al oxides are of importance. Diatomaceous earth is not considered to be very suitable. Finally Cu-containing Co catalysts were considered. They can be used without a preliminary reduction.

2234. Melan, G., and Weiss, B. Proof and Constitution of Branched Acids From Fischer-Gatsch Fatty Acids for Soap. I. G. Farbenindustrie A.-G., Ammonia Laboratory. FIAT Reel R–19, Frames 7160–7173, Feb. 14, 1942; PB 73,594; TOM Reel 25, Item 15, 1942, Frames 1460–1472; Standard Oil Development Co. Transl. Ella 2697, 1947. 10 pp.

Detailed method is described for determining the constitution of paraffin carboxylic acids, particularly those with branched chains. By treating with Br and MeOH, α–bromomethyl ester is produced from the carboxylic acid, and from this the α–hydroxyacid is purified. In the oxidative cleavage with lead tetraacetate and simultaneous flowing with air, CO_2 and an aldehyde are obtained from the hydroxyacid. The aldehyde is oxidized to a new carboxylic acid with one C atom less than in the starting material. In case of a branching in the α–position to the COOH group, a ketone is obtained instead of an aldehyde, which is not further oxidized. According to this method Fischer-Gatsch fatty acids for soap with C_{10} and C_{11} were examined and the fatty acids identified. The results are given in detail.

Melhorn, G. *See* abs. 1993.

2235. Meller, A. Catalytic Hydrogenation of CO–CH_4 Synthesis From Water Gas. Australian Chem. Inst. Jour. and Proc., vol. 10, 1943, pp. 100–114, 123–129; Chem. Abs., vol. 38, 1944, p. 238.

Laboratory and pilot plant experiments on the enrichment of CO–H_2 mixtures (ratios 3:5—1:2) are described. A catalyst containing 90% Ni and 10% Al_2O_3 gave high yields with 3:5 gas mixtures at 280° and a space velocity of 800–1,000 cm³ of gas per gm. of reduced catalyst per hr. Under these conditions the catalyst has a long life provided organic S compounds are absent. Higher temperatures and higher space velocities favor a side reaction associated with C deposition and decline of catalyst activity. Higher CO:H_2 ratios favor C deposition; lower ratios permit higher space velocities. S compounds decrease the active catalyst surface and cause C deposition. Lower CO:H_2 ratios enable the catalyst to resist higher concentrations of S. A 95–98% yield was obtained at a space velocity of 800–1,000 during a continuous run of 1,500 hr., when the organic S content was not greater than 0.5 grain per 100 cu. ft.

2236. Melville, H. W. Utilization of Coal for Oil Production. Catalytic Hydrogenation the Ideal Process. Petrol. Times, vol. 50, 1946, pp. 18, 43.

Digest of the Romanes lecture at the University of Aberdeen. Outstanding achievements in the treatment of coal to produce liquid fuels are high-pressure hydrogenation and Fischer-Tropsch synthesis. The first is undoubtedly the right way to obtain oil from coal; the degree of hydrogenation is easily controlled and final products can be worked up in the same way as petroleum. Economically, the disadvantage is the necessity for expensive equipment, and the problem is to find a simpler method of adding H_2. The Fischer-Tropsch synthesis needs the use of an excess of H_2, the expense of which weighs heavily against it and presents a fundamental difficulty that cannot be overcome. Costs of producing gasoline by various methods are as follows: High pressure hydrogenation 13 d. per imperial gal., Fischer-Tropsch from coal 11 d., Fischer-Tropsch from natural gas 5 d., high-pressure hydrogenation of petroleum 3.5 d., crude oil refined 3.5 d.

2237. Mengel, —. Continuous Chlorination of Kogasin and Recovery of Chlorine-Free Hydrochloric Acid. PB 758, 1942, 4 pp.

Continuous semicommercial production of chlorkogasin. (Lederoel Ho 1/90) is described in detail. Kogasin, a hydrocarbon mixture containing 6–8% unsaturates and an average molecular weight of 190–200 is chlorinated, HCl is removed, and the chlorinated product is stabilized by filtering through NaOH. The product has a consistency of machine oil and an average molecular weight of 320–330. It is a suitable substitute for train oil for the leather industry. Diagram of apparatus.

2238. Merck, F., and Wedekind, E. [Magnetic Analytic Investigation of Cobalt Oxide as Catalyzer of Carbon Monoxide Combustion at Room Temperature.] Ztschr. anorg. Chem., vol. 186, 1930, pp. 49–74; Chem. Abs., vol. 24, 1930, p. 2036.

It is concluded that the cobaltic oxide catalyzer consists essentially of 2 crystalline phases, CoOOH and Co_3O_4, Co_2O_3 being chiefly converted into the latter. Of these 3, the components CoOOH and Co_3O_4 are catalytically ineffective. The cobaltic oxide in the Co_3O_4 lattice is superfically reduced by the diluted CO. Magnetic measurements were made by Wedekind's microchemical method (*see* abs. 3619) and show that magnetism increases in going from hydrate to oxide. For Co_3O_4, χ is about 32×10^{-6} and varies relatively little as the titratable O content varies. In the transformation from hydrate to oxide, an active intermediate state is present, characterized by a dependence of susceptibility upon field strength. This vanishes on sintering and also on aging with partial reconversion into hydrate. At room temperature the hydrate is more stable than oxide$+H_2O$.

2239. Merkel, H. [Study of Fischer-Tropsch Iron Catalysts. I. Magnetic Investigation of Unused Iron Catalysts. II. Model Test With Copper Ferrite.] Brennstoff-Chem., vol. 31, 1950, pp. 208–212; Chem. Abs., vol. 44, 1950, p. 8564.

Fe catalysts with and without the addition of Cu were investigated thermomagnetically after precipitation and in different stages of drying at 105°. Directly after the precipitation, the precipitate appeared strongly ferromagnetic, yet its magnetization curve was still very irregular. After several hours of drying, Fe catalysts containing Cu gave uniform magnetization curves with a Curie point at 470°–475°. The intensity of magnetization was just as great as after the formation. If drying was continued for 29 hr. the Curie point, in spite of progressive oxidation of the constituents, remained virtually unchanged. The compound taken as a basis for the Curie point 470°–475° was no longer stable in the temperature range of the synthesis.

Heating to 220° for 3½ hr. resulted in complete decomposition whereby Fe_3O_4 in magnetically equivalent amounts appeared as the conversion product. Heating to 800° resulted in a sharp decline in the magnetization. By means of a model test it was seen that the compound taken as a basis for the Curie point 470°–475° had to do with a strongly ferromagnetic Cu ferrite whose magnetization curve still appeared after mild reduction conditions. In contrast to the behavior of Cu-containing Fe catalysts, a prepared Cu ferrite showed a sharp increase in magnetization after a heat treatment at 800°. This different behavior is due to the presence of oxidic iron in the catalyst after the ferrite formation, which does not appear magnetically. A Fe preparation without the addition of Cu showed after 8 hr. of drying, strong Fe_3O_4 formation. With progressive oxidation an increase in the Curie point was established. After a 30-hr. drying the Fe had been oxidized quantitatively into the trivalent form with formation of ferromagnetic Fe_2O_3. The Curie point of this oxide could not be accurately determined since the magnetization curve falls off almost linearly in the ferromagnetic conversion range. It lies in the temperature range of 600°–610°. Heating to 800° causes the loss of the magnetism of the Fe_2O_3, so that only the magnetism of the stable Fe_3O_4 remains. Beside the known effect of Cu on the forming and synthesis processes it is shown that this metal also influences the oxidation of Fe during the drying. By using Fe chloride for the initial solution, Cu-free materials easily form forremagnetic γ–Fe_2O_3 in quantitative amounts. In this condition the catalyst is difficult to reduce and cannot be used for the synthesis at normal pressure. On the other hand, ferritic combined α–FE_2O_3 is formed with extensive addition of Cu. Oxidation is thereby incomplete, 20–25% of the Fe remains in the bivalent form.

———. *See* abs. **2683, 2684, 2685.**

2239a. Merkel, H., and Weinrotter, F. [Thermomagnetic Studies of Iron Catalysts for Hydrocarbon Synthesis.] Brennstoff-Chem., vol. 32, 1951, pp. 289–297; Chem. Abs., vol. 46, 1952, p. 662.

When precipitated Fe catalysts are reduced with technical H_2, the low partial pressure of CO, CO_2 and CH_4 is sufficient to cause appreciable carbide formation. Catalysts treated in this way are fully active for synthesis in a few minutes, in contrast with those reduced with electrolytic H_2. In addition to Fe_2C with a Curie point of 265°, Fe_3O_4 and Fe were also found. the Fe content may be the cause of the CH_4 peak noted early in the synthesis. Since precipitated Fe catalysts can be converted into Fe_3C at temperatures >400° by means of technical H_2, without the formation of free C, there is a possibility of preparing pure cementite by reduction of Fe preparations containing no additives. This product was inactive as a catalyst. Metallic Fe is generally formed in the pretreatment of fused Fe catalysts with technical H_2. Carbides are only formed when additives favoring carbide formation (alkalies) are present; Fe_3C is formed due to the higher temperatures used.

2240. Merz, V., and Tibirica, J. [Synthesis of Formic Acid.] Ber. deut. chem. Gesell., vol. 10, 1877, p. 2117; vol. 13, 1880, pp. 23–33.

By passing CO over soda lime at 220°, formate is obtained in good yield. Above 220° the formate is decomposed with formation of carbonate and free H_2.

2240a. Messner, G., and Frankenburger, W. [Intermediate Compounds in the Catalytic Synthesis of Ammonia. Detection of the Formation of a Surface Nitride Between Nitrogen and Tungsten.] Ztschr. physik. Chem., Bodenstein-Festband, 1931, pp. 593–607; Chem. Abs., vol. 25, 1931, p. 5,515.

NH_3 and H_2 are adsorbed on W in the normal manner. N_2 apparently forms a surface compound with the W, since it is taken up irreversibly and in amounts that increase with the temperature. H is held similarly by chemical forces on a W surface already covered with N; the amount retained by the N-covered surface increases with temperature.

Metlin, S. *See* abs. **3655a, 3655b.**

2241. Meunier, J. [Oxidation Reactions of Methane.] Chim. et ind., vol. 60, No. 6, 1948, pp. 550–558; Chem. Age, vol. 60, 1949, pp. 293–296; Chem. Abs., vol. 43, 1949, p. 2923.

Oxidation reactions or the conversion of CH_4 into synthesis gas are assuming increasing industrial importance. These reactions, in which CH_4 is acted upon by O_2, steam, or CO_2 either alone or in binary or even ternary mixtures, are capable of being graphically represented by making use of the Gibbs triangle. When the reactions are effected in the presence of a catalyst, as is frequently the case, chemical equilibrium is quite easily attained. The author represents graphically the static conditions that may arise by thermal dissociation of CH_4 in the homogeneous phase as well as in the presence of C. Some typical cases are studied, and the effect of different factors, such as temperature, pressure, relative proportions of CH_4, and other reactants, is examined.

Meusel, A. *See* abs. **1030, 1031.**

2242. Meyer, A. J. P., and Taglang, P. [Magnetic Moments and Curie Points of Hexagonal and Cubic Cobalt.] Compt. rend., vol. 231, No. 13, 1950, pp. 612–614.

By methods and extrapolation, using isoelectronic cubic alloys of electron d. 27, Θ of hexagonal and M (magnetic moment in Bohr magnetons) of cubic Co, at obsolute zero, were determined. For hexagonal Co $\Theta=1{,}070°$ K. $M=1.70\ \mu_B$. For cubic Co $\Theta=1{,}404°$ K. packed, have 12 nearest neighbors, and have almost $M=1.745\ \mu_B$. Since both Co. structures are close identical shortest Co–Co distances (2.513 Å. for β–Co and 2.514 Å. for α–Co, the differences in Θ and M must be sought in interaction of not-closest neighboring atoms.

2243. Meyer, G., and Scheffer, F. E. C. [Carbide of Nickel.] Rec. trav. chim., vol. 46, 1927, pp. 1–7; Chem. Abs., vol. 21, 1927, p. 1236.

When CO is passed over Ni at approximately 250° for several hours, CO_2 and a carbide of Ni are formed. The existence of the latter is shown by its interaction with concentrated HCl to form hydrocarbons, which can be analyzed by ordinary methods. Combustion with CuO or by exploding a mixture of the hydrocarbons and O_2 gave identical results for CO_2, but the latter method gave lower values for H_2. This difference is ascribed to the presence of some unsaturated hydrocarbons. Experiments at 700° accord with the data on the dissociation of CH_4; no carbide is formed by the interaction of CO and Ni, and the carbide formed at lower temperatures is decomposed into Ni and C on heating at that temperature.

2244. ———. [Dissociation of Carbon Monoxide.] Rec. trav. chim., vol. 46, 1927, pp. 754–762; Chem. Abs., vol. 22, 1928, p. 714.

Equilibria were measured at 500°–750° by passing CO over a Ni catalyst. Equilibrium constants for $C+CO_2 \rightleftarrows 2CO$ are expressed by $\log K_c=(8{,}829/T)-7.067$ and $\log K_p=(9{,}217/T)-9.369$. True equilibria

were not obtained with a Ni catalyst until it was heated well above 420° to break up Ni carbide.

2245. ———. [Formation of Carbides in the Systems Metal–Carbon–Hydrogen and Metal–Carbon–Oxygen.] Rec. trav. chim., vol. 46, 1927, pp. 359–368; Chem. Abs., vol. 21, 1927, p. 3011.

Conditions for the existence of carbides in the systems M–C–O and M–C–H, in the presence of CO and CO_2, are discussed from the standpoint of the phase rule. Diagrams are given. Carbides rich in C and stable at low temperatures are probably formed during the reactions of water gas with metallic catalysts. A Ni carbide of the above type has been isolated.

2246. ———. [Formation of Carbides in the System Metal–Carbon–Oxygen.] Rec. trav. chim., vol. 47, 1928, pp. 401–405 (in French); Chem. Abs., vol. 22, 1928, p. 1919.

Theoretical considerations are augmented. The knowledge of the values of the heats of formation of the different equilibria helps to determine to which one of the 4 types of P–T diagrams a certain system belongs. The system Ni–C–O is taken as an example to prove the conclusions.

2247. ———. [Water-Gas Equilibrium.] Rec. trav. chim., vol. 57, 1938, pp. 604–608; Chem. Abs., vol. 32, 1938, p. 8246.

Direct determinations of the constant of the water-gas equilibrium at different temperatures led to the formula $\log K=-(1860/T)+1.662$. By means of an indirect method, a slightly different result was obtained: $\log K=-(1881/T)+1.705$. The average of the 2 gives: $\mathrm{Log}\ K=-(1870/T)+1.683$.

2248. Meyer, H. H. [Speed of Reduction of Iron Ores in Flowing Gases.] Mitt. Kaiser Wilhelm Inst. Eisenforsch. Düsseldorf, vol. 10, 1928, pp. 107–116. Chem. Abs., vol. 23, 1929, p. 1371.

At 650° the ores reduced in H_2 begin to sinter, and H diffuses less readily to the center of the kernels. As a result, the speed of reduction falls rather sharply. At 900°, the speed is again accelerated, since H diffuses more rapidly into the γ–Fe. In CO, sintering is effectively prevented by the separation of C. The speed of reduction, however, is slower than with H_2 so long as there is no sintering. For technical purposes a mixture of CO and H_2 is very effective, because of the reactivity of the H_2 and the prevention of sintering by the CO. Magnesite reduces chiefly on the surface, and the higher the temperature the greater must the degree of reduction be before C is set free. The presence of H_2 promotes C formation. With minette (Fe silicate) the phenomena are the same, but because of its greater porosity the reduction is more rapid. Likewise the separation of C in the interior of the kernel tends to break it up. Above 1,000° silicates are formed that close up the pores and retard the reaction. Where no sintering occurs the speed of reduction is about 4 times greater with H_2, and in both cases the speed is proportional to the surface of the ore and the concentration of the gas, the reaction velocity constant being d/D, where d is the diffusion coefficient and D is the thickness of the adsorbed gas layer. The temperature coefficient of the speed of reaction is consequently quite small. In H_2–CO mixtures, the CO does not appear to reduce directly, but converts the H_2O formed into H_2 and CO_2.

Meyer, K. *See* abs. **988, 989, 990, 991, 992, 993, 1048, 2622, 3070, 3071, 3072.**

2249. Meyer, K., and Horn, O. [Reaction of Carbon Monoxide and Hydrogen in Coke-Oven Gas With Molybdenum Catalysts.] Ges. Abhandl. Kenntnis Kohle, vol. 11, 1934, pp. 389–394; Chem. Zentralb., 1934, II, p. 875; Chem. Abs., vol. 29, 1935, p. 6732.

No reduction of CO occurs at 1 atm. At 100 atm. reduction to CH_4 occurs, but a higher temperature (400°) is needed with a Mo than with a Ni catalyst. Mo is activated by Mn, Cr, Th, and Cu but not by W. Alkali destroys the activity. Mo and Mo–Th catalysts for the hydrogenation of C_2H_4 are not poisoned by H_2S.

2250. Meyer, R. E. Petroleum Products vs. Petroleum Chemicals. Chem. Eng. News, vol. 28, 1950, pp. 1906–1910.

Discussion is made of the production of petroleum chemicals such as light hydrocarbons (liquid petroleum gases), nylon and acrylonitrile plastics, acetylene products, hydrocarbon oxidation products, such as acrolein, phthalic anhydride, phenol from benzol, ethylene oxide and ethylene glycol, and products of the Fischer-Tropsch synthesis and the Oxo process. The utilization of the large quantities of byproducts from these 2 processes and their separation and purification are definitely unsolved problems and it cannot yet be foreseen what the effect will be on the chemical markets and the price structure.

2251. Meyer, W. [Technical Progress in the Production of Fatty Acids and Alcohols From Hydrocarbons.] Pharm. Ztg., vol. 82, 1937, pp. 1189–1194; Chem. Zentralb., 1938, I, p. 1659; Chem. Abs., vol. 32, 1938, p. 1652.

Review with 112 refs.

2252. ———. [Review of the Development of the Oxidation of Hydrocarbons to Fat Acids, Fat Alcohols, and Wax Esters.] Seifensieder-Ztg., vol. 65, 1938, pp. 215–217, 238–239, 256–258, 277–278, 297–299, 317–319, 338–340. Süddeut. Apoth. Ztg., vol. 78, 1938, pp. 47–49; Chem. Abs., vol. 32, 1938, p. 9532.

Oxidation methods using atmospheric O_2 various oxidizing compounds, for example, oxides of N_2, O_3, etc., are considered in this review citing 283 refs.

2253. ———. [Soap From Coal.] Süddeut. Apoth.-Ztg., vol. 78, 1938, pp. 47–49; Chem. Abs., vol. 32, 1938, p. 2770.

Brief outline of various methods and suggestions looking to the technical production of fatty acids and alcohols from hydrocarbons through oxidation of unsaturated hydrocarbons with atomic and molecular O and O_3, combination of olefin formation and oxidation, and finally oxidation of saturated hydrocarbons by combined O and molecular O_2.

2254. Meyer, W. F. [Investigations of Cobalt and the System Cobalt–Carbon.] Ztschr. Krist., vol. 97, 1937, pp. 145–169; Chem. Abs., vol. 31, 1937, p. 8339.

X-ray photographs at temperatures up to 1,100° show no 2d transformation of Co. On heating with illuminating gas up to 230°–270° a mixed crystal of variable composition is formed, which is unstable at room temperature. At 500°–800° stable Co_3C is formed, analogous to Fe_3C. Its unit cell dimensions are $a=4.52$, $b=5.08$, $c=6.73$ Å. Heating with benine and CO also produces Co_3C.

2255. ———. [Cobalt–Carbon System.] Metallwirtschaft vol. 17, 1938, pp. 413–416; Chem. Abs. vol. 32, 1938, p. 4866.

When illuminating gas is heated with Co in the temperature range 230°–470° the CO dissociates under the catalyzing effect of Co and a mixed crystal forms. The crystal is attainable only between 230° and 270°, when a diffusion equilibrium exists; above this range the outward diffusion of C is too rapid. Between 500° and 1,200°, Co also catalyzes CO dissociation and a mixed crystal forms. Between 500° and 800°, benzene as well as illuminating gas acts on Co to form a stable Co carbide, whose lattice structure corresponds to that of Fe_3C; the lattice dimensions, to an accuracy of ±0.5% are: $a=4.52$ Å., $b=5.08$ Å., $c=6.73$ Å. 11 refs.

———. *See* abs. **1935.**

2256. MEYER-DOERING, H. H. [Is the Use of Synthetic Fatty Acids for Food Dangerous?] Klin. Wochschr., vol. 27, 1949, pp. 113–116; Chim. et ind., vol. 63, 1950, p. 159; Chem. Abs., vol. 44, 1950, p. 4161.

Paraffinic products obtained by the Fischer-Tropsch process can be partly converted into fatty acids by oxidation in presence of appropriate catalysts such as Mn and Co. A mixture of fatty acids is obtained containing 55% of products having more than 10 C atoms, 20–25% with less than 10 C atoms, of which 50% are HCOOH, CH_3COOH, and CH_3CH_2COOH, besides esters, anhydrides, lactones, ketones, etc. The mixture is saponified by soda, and the C_{10}–C_{23} acids are precipitated and separated from the unsaponifiable constituents by distillation and esterified to fatty acids with glycerin. It would seem that such acids would not be free from danger. In fact they may contain isoacids, which have a marked toxic action. The presence of dicarboxylic acids may likewise cause trouble, as well as the synthetic or fermentation glycerin used for the esterification. It appears then that the use of artificial fats must be considered dangerous. The following considerations are against the use of synthetic fats for food: (1) There is no published procedure for the determination of isofatty acids, certain of which are definitely toxic; (2) there is no specific method for determining dibasic acids in fats; (3) the many animal experiments that have been cited do not prove the harmlessness of the fats, unsuitable experimental animals were used, the experiments were too short, and improper methods were used for studying liver or kidney damage; (4) there is an increase in excretion of dibasic acids, a strong acidity of the urine, and the possibility of kidney damage in human subjects; (5) in human experiments with synthetic fats, their harmlessness was not shown since the experiments were too short, not enough chemical methods were used, and common clinical methods were often neglected; (6) the metabolism of the odd-numbered fatty acids is still not clear.

MEYERSON, S. *See* abs. 2754a, 3618.

2257. MICHAEL, —. [Hydrocarbon Synthesis From Carbon Monoxide and Hydrogen.] TOM Reel 148, frames 99–102, Aug. 14, 1942, 5 pp.

Emulsion method consists in carrying out the reaction in a sludge characterized by very small particles of gas and catalyst. As sludge the high-boiling reaction products are used. Gas distribution was produced by foam stones with pores of 0.10–0.15 mm. diam. The catalyst can also be fixed in place by using finely divided metal 1–5 μ particle size in a heavy sludge. In order to counteract a sinking of the catalyst particles and to conduct away the heat of reaction, the heavy sludge is slowly agitated between the reactor and the cooler so that the heavy emulsion has an opportunity to be degassed at the highest point in the circulation system. Temperatures of 240°–280° can be used, usually 250°. Exact conditions and materials to be used are given.

2258. ———. [Status of Experiments on Synthetic Oils.] TOM Reel 148, frames 244–249, June 1, 1942, 5 pp.

Experiments have been continued on the foam process with ovens of various capacities. Intensive stirring was tried in place of the foam plates, but difficulty arose at the stuffing boxes of the stirring well so the tests were discontinued. Details of the oven construction are given. Describes catalyst, its suspension in oil, and its regeneration. The conditions for operation of the ovens are: 20 atm. pressure, CO : H_2=55 : 45, temperatures 250°–280°. Foam plates containing sulfate must not be used. Quartz and glass powder plates of 0.1 and 0.2 mm. pore diam. were used, but were found to be too sensitive to thermal expansion on a large scale. Chamotte plates are preferred.

2259. ———. [Status to Date of Hydrocarbon Synthesis According to the Emulsion Method.] TOM Reel 148, frames 235–241, May 18, 1942, 5 pp.

Emulsion method using a 1.5 $m.^3$ oven has not shown any technical difficulties. There is no doubt that also in an industrial plant, using ovens of 40–50 $m.^3$ capacity, the same results would be obtained. The essential parts of the plant are shown. Chamotte-stones are used as porous foam stones. In using an oven 8 m. high, the correct pore diameter is 0.15 mm. It has not been found whether the 8-m. oven is the right one to use, and tests are being extended. A relation exists between the fineness of the foam and the yield and also between the fineness of the foam and the height of the oven.

2260. MICHAEL, J. M., AND HAGER, K. F. Corrosion-Inhibited Fuels. Ind. Eng. Chem., vol. 41, 1949, pp. 2616–2622.

Methods for preventing corrosion in pipelines, storage containers, tanks, and other equipment in contact with fuels even under severe conditions are surveyed. Of the possibilities investigated, only the admixture to the fuels of corrosion inhibitors to produce surface passivity offers extended technical application and enough endurance in practical use. The data presented show that fuels inhibited by hydrocarbon-sulfamido-carboxylic acids offer the greatest advantage. Extensive investigations on emulsifying agents led to the surprising result that, without regard to the construction materials used, even a small addition of the Na salt of Mepasin-sulfamido-acetic acid to the fuel prevents any corrosion. Mepasin is a high-boiling fraction of the hydrocarbons obtained by the Fischer-Tropsch synthesis having a chain length of about 12–18 C atoms. A mixture of about equal parts of Mepasin-sulfamido-sodium acetate and unchanged Mepasin is a very efficient emulsifier known in Germany under the trade name Bohrmittel Hoechst.

2261. MICHAEL, W. Experience With the Synthesis Reactor Stall 506. June 28, 1941. Bureau of Mines Transl. T–434, January 1948, 5 pp., incl. 3 figs.

Paper from Dr. Pier's files, discussing gas circulation versus the foaming process in reactor operation.

2262. MICHAEL, W. Present Status of the Synthetic Oil Experiments, Jan. 6, 1942. Bureau of Mines Transl. T–439, Jan. 1948, 6 pp.

Foam synthesis method has been adapted to industrial production by placing in operation a 1.5 $m.^3$ capacity reactor provided with a foam plate, made of chamotte or quartz with sintered powdered glass with pores 0.1–0.2 mm. diameter, for the distribution of the synthesis gas. Stirring methods had to be discontinued because of difficulties in the stuffing boxes of the mixer shaft. The reactor apparatus consists of a vessel near the bottom with a perforated foam plate and a degasifier at the head of the reactor in which the rising foam gives up its gas, the liquid being returned by an outside line to the bottom of the reactor and recirculated under such a pressure (about 20 atm.) as to counteract the tendency of the powdered catalyst to settle. The rate of circulation is further determined by the need of removing the heat of reaction in the liquid phase by a cooler located in the reactor jacket. For example, with a temperature rise of the liquid of 10°, the liquid would need to circulate at a synthesis temperature of 250° at the rate of once every 3 min. Oil is used as the intermediate cooling agent surrounding the reactor and is pumped in a circuit through the cooler. The catalyst consists of Fe from Fe oxide obtained by burning Fe carbonyl, pasted with a solution of potassium borate, dried, reduced in H_2 at 450°, and ground in heavy oil to a particle size 1–5 μ. The amount of catalyst is 300–400 kg. per $m.^3$ of the liquid, the dispersion medium being the high-boiling fraction obtained in the synthesis. The synthesis is performed under pressure, at 250°–300°, with a synthesis gas CO : H_2 : : 55 : 45. The space-time yield of products range from 0.2–0.3 kg. per l. catalyst space per day at 250° to 0.7–0.8 kg. at 300° with a conversion of 80 to even 95% of the gas by purifying the recycle gas from CO_2. The compositions of the products in % at 250° and 300°, respectively, are as follows: Gasol, 4–6 and 8; gasoline boiling at 200°, 30–40 and 50–55; middle oil boiling at 350°, 32–37 and 30–35; paraffin above 350°, 20–30 and 5–10; alcohols, 6 and 3; octane number of gasoline, 50 and 78; olefins in middle oil, 60 and —; gasification, 5 and 5.

2263. ———. Principal Data on the Foaming Process for the Hydrocarbon Synthesis. High-Pressure Experiments, Ludwigshafen 558, Feb. 27, 1943. Bureau of Mines Transl. T–431, January 1948, 2 pp.

Paper from Dr. Pier's files outlining the operation and giving some results and yields of experiments carried out over a 7-mo. period.

2264. MICHAEL, W., AND EHRMANN, —. Difficulties Encountered in the Foaming Method of Synthesis of Hydrocarbons and Their Solution. High-Pressure Experiments, Ludwigshafen 558, Feb. 18, 1943. Bureau of Mines Transl. T–432, Jan. 1948, 7 pp.

Paper from Dr. Pier's files. No fundamental difficulties have been encountered in large-scale experimental work on the foaming process, and no important unsolved problems remain. Any troubles encountered were caused by stuffing boxes, chiefly of rapidly rotating shafts, and by the sticking of the catalyst to the walls in the sump and gas spaces and could be overcome by relatively simple measures.

2265. ———. Deposition of Finely Divided Catalysts on the Reactor Walls in the Foam Process, Jan. 5, 1944. Bureau of Mines Transl. T–438, January 1948, 12 pp.

Paper from Dr. Pier's files on high-pressure experiments, Leuna. A peculiar phenomenon is observed in the foam process of hydrocarbon synthesis in the disappearance of the catalyst in the liquid phase and its deposition on the reactor walls, increasing from bottom to top. It is undesirable in that it prevents the full performance of the catalyst and reduces the available reaction space. It is thought to be due (and an analysis gives credence to the idea) to an increasing concentration of CO_2 and steam in the upper part of the reactor and the formation of $FeCO_3$.

2266. MICHAELIS, P. [Development of Coal Processing. I. Coal as a Source of Solid Products.] Oel u. Kohle, vol. 37, 1941, pp. 701–705; Chem. Zentralb., 1942, I, p. 137; Chem. Abs., vol. 37, 1943, p. 5845.

Review of the processing of coal; the use of coke for the manufacture of carbides and C_2H_2, and the chemical products derived from it; low-temperature carbonization of coal; the preparation of briquets and cleaned coal and the uses of the latter; and the classification, properties, and uses of coal according to age and seam.

2267. ———. [Development of the Conversion of Coal. II. Coal as a Source of Liquid Products.] Oel u. Kohle, vol. 37, 1941, pp. 851–858; Chem. Abs., vol. 36, 1942, p. 3025.

Different known processes—for example, coking, tar, distillation, phenol, and benzene production—are discussed, and tables of the properties of the obtained products are given.

2268. ———. [Development of the Conversion of Coal. III. Coal as a Raw Material for Gaseous Products.] Oel u. Kohle, vol. 37, 1941, pp. 949–955; Chem. Abs., vol. 37, 1943, p. 3584.

Review of 79 German papers on coal-gas production, processing, and uses, published from 1926–41, outlines briefly the production of city gas; such gas purification methods as the Alkazid, Thylox, Polythionate, and Katasulf processes; recovery of H_2S, and NH_3 from coal gas; production of water gas; and production of hydrocarbons and O-containing organic compounds by the Fischer-Tropsch process.

2269. MICHEL, A. Magnetic Properties of Some Solid Solutions.] Ann. chim., vol. 8, 1937, pp. 317–423; Chem. Abs., vol. 32, 1938, p. 1989.

First part of this monograph gives the results obtained by thermomagnetic studies on α–Fe_2O_3, $Fe_2O_3 \cdot BaO$, $Fe_2O_3 \cdot SrO$, $Fe_2O_3 \cdot PbO$, the cubic sesquioxide of Fe, and the ferrites of Ni, Mg, and Cu. The effects of method of crystallization and grain size are discussed. In Part II the results are given for solid solutions of α–Fe_2O_3 in F_3O_4, Fe_3O_4 in α–Fe_2O_3, mixtures of rhombic sesquioxide with cubic sesquioxide, solid solutions of magnetite and the ferrites of Ba, Sr, and Ca, the unstable ferrites of Be, and the ferrites of Ag, Hg, and Li. Part III gives the results of a similar study of pyrrhotite, and solid solutions of FeS with S, Si, As, Te, Ti, W, Co, Ni, Cu, Zn, Sb, Mn, Ag, Fe, Cd, Pb, and Bi. The general significance of the results and the interpretation of the anomalies in the temperature-magnetization curves are discussed. Extensive bibliography appended to each part.

2270. ———. [Substitutions in Magnetite and Preparation of New Cubic Sesquioxides of Iron.] Bull. Soc. chim. France, 1949, D128–D131; Chem. Abs., vol. 44, 1950, p. 17.

Preparation of magnetite is described in which a bivalent Fe ion is replaced by K, Na, Mn, or Mg, and a trivalent Fe ion is replaced by Al or Cr. Variation of parameters and of the Curie point is given for these substituted magnetites and for the cubic sesquioxides obtained by heating. Temperatures of transformation for cubic $(Fe_{1-x}Al_x)_2O_3$ are: for x=0~450°; for x=0.03 610°–615°; for x=0.09~650°. Thermomagnetic analysis revealed significant differences between the heating and cooling period. These differences increase, but Curie point for both periods decrease, at higher Al_2O_3 contents. Al_2O_3 stabilizes the cubic form of the sesquioxides. The cubic structure of $(Fe,Al)_2O_3$ is obtained also by calcination of the nitrates and to some extent by calcination of the sulfates.

2270a. ———. [Application of Thermomagnetic Analyses to the Study of Catalysts.] Ind. chim. belge, vol. 17, 1952, pp. 643–651; Chem. Abs., vol. 47, 1953, p. 31.

Relation betwen the thermomagnetic and catalytic properties of Fe, Ni and Co catalysts for Fischer hydrocarbon synthesis (CO+2 H_2) was studied (a) for a variety of conditions of catalyst preparations and (b) with several catalyst promoters. In general, good catalysts exhibited a distinct type of thermomagnetic curve. However, this relation should not be unduly emphasized until more is known about other properties that are responsible for catalysis.

———. *See* abs. 209, 742a, 743, 1279, 2076.

2271. MICHEL, A., AND BERNIER, R. [Thermomagnetic Study of Cementite Stability.] Rev. mét., vol. 46, 1949, pp. 821–824; Chem. Abs., vol. 44, 1950, p. 1868.

Cementite was prepared by passing a mixture of CO and 2 H_2 over spectroscopically pure Fe oxide held at 560°–1,000°. Thermomagnetic analysis of this Fe_3C showed its Curie point at 210° and its comparative stability under conditions of thermal testing. About ⅓ of cementite is graphitized when heated for 15 hr. in vacuum at 825°, and heating at 900° destroys ⅔ of it. Heating both in H_2 and in N_2 rapidly decomposes this cementite.

2272. MICHEL, A., AND CHAUDRON, G. [Stabilized Cubic Ferric Oxide.] Compt. rend., vol. 201, 1935, pp. 1191–1193; Chem. Abs., vol. 30, 1936, p. 692.

Solid solutions of varying amounts of $NaFeO_2$ in Fe_2O_3 were prepared by adding various amounts of aqueous NaOH to precipitated $Fe(OH)_3$, the product being reduced to Fe_3O_4, oxidized at 300° and then heated to 650°. The Curie point decreased regularly with increasing content of Na_2O, while the side of the unit cube (*a*) increased with equal regularity, the figures for an oxide containing about 5% Na_2O being about 400° and 8.52 Å., and (by extrapolation) 675° and 8.32 Å. for pure Fe_2O_3. The dissociability of Fe_2O_3 (into Fe_3O_4 and O_2) decreases rapidly with increase in Na_2O, and with 5% thereof it is virtually undissociable at 300°. Though the content of Na_2O is reduced by hydrolysis in hot H_2O or by AcOH, no change in Curie point or *a* occurs until after reheating to 650°. Solid solutions of other ferrites behave similarly, the limit solutions of those of Be, Ag, and K having Curie points at 220°, 270°, and 250°, respectively.

2273. Michel, A., and Gallissot, M. [Thermomagnetic Anomaly at Ordinary Temperatures in Microcrystalline Ferromagnetic Substances.] Compt. rend., vol. 207, 1938, pp. 140–142; Chem. Abs., vol. 32, 1938, p. 6919.

Cause of the anomaly in the magnetization: temperature curves of various ferromagnetic substances, Fe_2O_3 and various ferrites, according to the state of crystallization, are discussed, and the explanation is suggested that the Curie points of the minute crystallites in the microcrystalline varieties vary, being lower the smaller the crystallite, but always above 20°, below which the normal law is followed. Thus a hyperbolic form of curve may be due to physical as well as chemical heterogeneity.

2274. Michel, A., and Pouillard, E. [New Family of Cubic Iron Sesquioxides.] Compt. rend., vol. 228, 1949, pp. 680–681; Bull. soc. chim. France, 1949, p. 152; Chem. Abs., vol. 43, 1949, p. 8934.

Mixed crystals of cubic $(Fe_{1-x}Al_x)_2O_3$ were obtained by oxidation of magnetite, $x(Al_2O_3)$ $(1-x)Fe_2O_3.FeO$, in which Fe^{+++} ions are partly substituted by Al^{+++} ions. The limit of solution is near to 10% Al_2O_3 at room temperature. The parameter of the lattice decreases from 8.324 Å. for cubic Fe_2O_3 to the value 8.20 Å. continuously. The solubility of Al_2O_3 increases at higher temperature. The content of Al_2O_3 stabilizes the cubic form. The temperature of quick transformation from the cubic form into the rhombohedral form is 200° for pure Fe_2O_3, 610° for the substitution $x=0.03$, and 650° for the substitution $x=0.07$. A stabilized cubic mixture with 32% Al_2O_3 was obtained by quenching from 600°; its Curie point was 410°. No modification in the stability of cubic Fe_2O_3 was obtained by Cr_2O_3, since it is insoluble in Fe_2O_3.

2275. Michel, A., Benard, J., and Chaudron, G. [Mechanism of the Superficial Oxidation of Iron.] Bull. soc. chim., vol. 11, 1944, pp. 175–179; Chem. Abs., vol. 40, 1946, p. 2370.

Specimens of electrolytic Fe were heated at temperatures from 250°–900° in air. The structure of the separated oxide scale was determined by use of the Debye-Scherrer method of X-ray diffraction and the thermomagnetic method of analysis. At 250°, the oxide consists largely of γ Fe_2O_3 and a small quantity of Fe_3O_4. The reaction mechanism is given by the equation $Fe \rightarrow Fe_3O_4 \rightarrow \gamma\text{–}Fe_2O_3$. In the interval of 400°–600° variable mixtures of γ Fe_2O_3 and Fe_3O_4 are formed. The mechanism is given by the equation $Fe \rightarrow Fe_3O_4 \rightarrow \gamma\text{–}Fe_2O_3 \rightarrow \alpha\text{–}Fe_2O_3$. Above 600° FeO is the major component. At 900° after 3 hr. of oxidation and a rapid cooling the oxide consists largely of FeO. A small quantity of Fe_3O_4 is found in the superficial layer and a film of $\alpha\text{–}Fe_2O_3$ on the surface. The mechanism of oxidation is $Fe \rightarrow FeO \rightarrow Fe_3O_4 \rightarrow \alpha\text{–}Fe_2O_3$. The FeO is assumed to decompose on cooling by the reaction $4FeO \rightarrow Fe_3O_4 + Fe$. It is concluded that both Fe and O_2 diffuse in the oxidation reaction. The distribution of reaction products is determined by the magnitude of each process.

2276. Michel, A., Bernier, R., and LeClerc, G. [Thermomagnetic Study of Fischer Catalyst Containing Nickel.] Jour. chim. phys., vol. 47, 1950, pp. 269–273; Chem. Abs., vol. 44, 1950, p. 7638.

Results of a thermomagnetic and structural study of Ni catalysts. An intimate relation existed between the catalytic activity of Ni and the crystal size. The most active catalysts possessed a certain type of magnetization-temperature curve that was correlated by means of X-rays with the crystal size. Under certain conditions of catalysis, the Ni catalyst was transformed into a paramagnetic hexagonal carbide of Ni. In the initial stages of catalysis the C formed a solid solution with the Ni and expanded the face-centered cubic structure. The lowering of the Curie point of active Ni catalysts after use for 100 hr. suggested that small amounts of C were present in these catalysts.

2277. Michot-Dupont, F. [Treatment of Imperfect Fuels by Methylation to Obtain Aromatic Fuels.] Cong. mondial pétrole, 2me Cong., vol. 2, 1937, pp. 197–212.

Michot-Dupont methylation-distillation method for producing aromatic fuels is reviewed with regard to the features of the process, the constitution and utilization of the products, yields, starting materials, industrial application, reaction mechanism,, temperature study, initial costs, comparison with other low-temperature processes, sulfur recovery, and use of salts other than acetates.

Mickelson, H. G. *See* abs. 1488.

2278. Mignolet, J. [Investigations on Adsorption at Present in Progress.] Rev. univ. mines, vol. 19, 1943, pp. 111–113; Chem. Zentralb., 1943, II, pp. 1781–1782; Chem. Abs., vol. 38, 1944, p. 5719.

Adsorption of H_2 on catalysts of MoO_2 base is being investigated. Contrary to the results of other authors this oxide has not been found to be stable in the presence of H_2. In the temperature range in which Mignolet worked, a slow reduction of the MoO_2 was observed, and it is now the aim to find the reduced form stable under conditions suitable for the technical use of MoO_2. The apparatus used in the experiments is described.

2279. Miller, A. E. Motor Fuel From Coal—Description of the Recent Work of Bergius, Fischer, and Patart. Bull. Am. Petrol. Inst., vol 8, No. 6, 1927, pp. 152–159; Petroleum (London), vol. 24, 1928, pp. 103–105, 139–141; Chem. Abs., vol. 21, 1927, p. 1532.

Processes of Bergius, of Badische Anilin-u. Soda-Fabrik, of Fischer-Tropsch, and of Patart are described. Bibliography of 130 refs.

2280. Miller, B. [Active Carbon Recovery of Gasoline in the Fischer-Tropsch Process.]. Apparatebau, vol. 50, 1938, pp. 97–98.

Steps in the operation and costs.

2281. ———. Chemical Utilization of Natural Gas. Petrol. Refiner, vol. 24, No. 5, 1945, pp. 121–124; Petroleum Eng., vol. 16, No. 8, 1945, pp. 216, 218, 220, 222, 224, 226, 228; Nat. Petrol. News, vol. 37, No. 23, 1945, pp. R–430, 432–434, 436; Oil Weekly, vol. 117, Apr. 30, 1945, pp. 50–54.

After a discussion of the uses of natural gas in the production of He, C black, synthetic NH_3, natural gasoline, synthetic rubber, plastics, and MeOH, attention is directed to the Fischer-Tropsch process as offering a means of converting natural gas into liquid hydrocarbons suitable for motor fuel, supplying a market that could absorb the entire natural-gas production. It is pointed out that if improvements now thought profitable in this field should be realized, natural gas would become a more economical source of motor fuel than petroleum.

2282. ———. Synthetic Liquid Fuels and the Manufactured-Gas Industry. Gas Age, vol. 97, No. 4, 1946, pp. 19–21, 68.

Discussion of means whereby the synthesis gas industry and the manufactured gas industry can be made complementary with the view of creating another source of city-gas production. It is not thought that the production of synthetic liquid fuels from natural gas can be considered a permanent solution of the problem of supply if and when our petroleum is exhausted; only coal is available in enough quantity to offer a solution of the problem. If the Fischer process is to be operated on coal economically, a process must be developed for production of synthesis gas from low-grade coals. It is suggested that the gas industry supply the process and the equipment to carbonize low-grade coal for gas and char production and sell the char to the synthetic liquid-fuel industry for the manufacture of water gas and synthetic gasoline, turning back to the manufactured gas industry the residual liquid products from the refining of the synthetic gasoline to be used as carburetting material for city gas. Continued research in the field of synthetic liquid fuels is almost certain to bring forth improvements that can be applied in the gas industry, and the latter can look with optimism upon such developments.

Miller, G. H. *See* abs. 2993.

2283. Millett, H. C. Lurgi Process for Complete Gasification of Coal With Oxygen Under Pressure. Jour. Inst. Fuel, vol. 10, 1936, pp. 15–21; Chem. Abs., vol. 31, 1937, p. 3238.

Large-scale experimental plant is described. The generator consists of a cylindrical shaft with an effective cross-sectional area of 10.4 sq. ft. operating with a fuel bed 10 ft. deep. With lignite, a daily output of 700,000 cu. ft. of gas was obtained. With a mixture of steam and O_2 under 20–30 atm. pressure, a gas comparable, after simple purification, with normal town's gas was obtained. It is possible to obtain by this process a high output of gas from a small plant. The successful operation of the high-pressure gasification process is shown to depend on the obtaining of the correct balance between the rate of production of CH_4 and the rate of gasification of coke in steam.

———. *See* abs. 691, 692, 693, 694.

Milligan, W. O. *See* abs. 3635, 3636.

2284. Milligan, W. O., and Holmes, J. X-Ray Diffraction Studies in the System $CuO\text{–}Fe_2O_3$. Jour. Am. Chem. Soc., vol. 63, 1941, pp. 149–150; Chem. Abs., vol. 35, 1941, p. 1336.

Report of the results of a systematic X-ray study of mixtures of varying composition of cupric and ferric oxides, which were precipitated at 25°, aged under water at 100°, and heated to 1,000°. The radiograms show no indication of the formation of cupric ferrite on precipitation at 25° or on aging the precipitate at 100°. In the samples heated to 1,000°, $CuFe_2O_4$ is formed; it is the only compound formed in the system $CuO\text{–}Fe_2O_3$.

2285. Mills, G. A., Boedeker, E. R., and Oblad, A. G. Chemical Characterization of Catalysts. I. Poisoning of Cracking Catalysts by Nitrogen Compounds and Potassium Ion. Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1554–1560; Chem. Abs., vol. 44, 1950, p. 6611.

Basic organic N compounds, such as quinoline, are held on $SiO_2\text{–}Al_2O_3$ ($-MgO$, $-ZrO_2$) catalyst surfaces by physical and chemical forces. These forces are widely different so that at 250°–500° the physically held quinoline can be distinguished from that chemically held. At a given temperature, the amount of physically held N compound is increased with an increase in its partial pressure. The amount chemisorbed is decreased with an increase in temperature. The cracking activity of the catalysts studied was proportional to their capacity to chemisorb quinoline at cracking temperatures. Catalysts that have basic N compounds chemisorbed or that have K added by base exchange are poisoned for cracking. From a study of partial poisoning an exponential relationship was found between the amount of certain N compounds chemisorbed and the yield of C_6H_6 from the dealkylation of cumene. A relatively small fraction of the total surface of SiO_2-metal oxide cracking catalysts is responsible for catalytic activity. The chemical properties exhibited by this part of the surface identify the active principal as an acid.

Minachev, K. M. *See* abs. 3179.

2286. Minchin, L. T. Liquid Purification—Some British and Continental Developments. Coke and Gas, vol. 13, 1951, pp. 27–29.

Some of the more recent processes and plant for removal of H_2S from town gas or coke-oven gas by liquid reagents are described: The Dutch State Mines-Otto process, which uses a washing liquid containing initially ferrous sulfate and potassium ferrocyanide; the Collin process installed at Duisburg in the Ruhr district of Germany using NH_3 liquor of about 6 oz. strength in the form of a spray; the Szombathy process, which uses an aqueous solution of sodium thiosulfate and a water-soluble catalyst (not given), which functions as an O carrier and oxidizes the H_2S to H_2O and S. The H. Koppers Co. owns the patents. Test results are not yet available. A full-scale plant to deal with 7 million cu. ft./day is under construction.

2287. Mining and Metallurgy. Liquid-Fuel Production by Hydrogenation Today. Vol. 17, 1936, pp. 439–440; Chem. Abs., vol. 30, 1936, p. 8570.

Sketch of development of pressure hydrogenation and economic possibilities of satisfying the world's gasoline requirements.

Miroshnichenko, G. K. *See* abs. 846.

Mishima, A. *See* abs. 1916, 1917.

2288. Mitchell, J. A. Organic Catalytic Reactions. Jour. Chem. Education, vol. 9, 1932, pp. 59–71; Chem. Abs., vol. 26, 1932, p. 1235.

Complete survey of the development of the MeOH process and synthesis of higher alcohols from CO and H_2, a discussion of oxidation of cyclic compounds to produce maleic anhydride, phthalic anhydride and anthraquinone. Gives extensive bibliography of articles in English.

2289. Mitchell, R. Petroleum Reprieve. Wisconsin Eng., vol. 52, No. 2, 1947, pp. 10, 32; Chem. Abs., vol. 42, 1948, p. 5201.

Production of cheap O_2 has made the Fischer-Tropsch process for producing synthetic hydrocarbons practical in America. The development of the fluid-bed catalyst reactor has improved quality. By controlling the rate of heat removal from the reacting constituents, different properties can be given to the product.

2290. Mitchell, R. F. Oxygen-Steam Producer Blast. Canadian Chem. Process Ind., vol. 30, No. 8, 1946, pp. 34–42.

Deals with the O_2-steam gasification of coke at atmospheric pressure in Wellman-Galusha clean gas generators for the production of gas for NH_3 synthesis at Trail, British Columbia, Canada. Reports brief survey of early investigations on the use of an O_2 steam blast, and briefly describes 4 processes: Lurgi, Winkler, Thyssen-Galoczy, and Abstich (slagging) producers.

———. *See* abs. 3744.

2291. Mitsui, K. Summary of Research on the Conversion of Coal to Oil at the First Naval Fuel Depot, Ofuna. U. S. Naval Tech. Mission to Japan, X-38 (N)-7, Encl. (A), 1945, pp. 31–36; PB 58,701.

Summary of studies leading up to operation of the Bergius and Fischer-Tropsch processes for the synthesis of liquid fuel from coal in Japan.

2292. Mittasch, A. [Contact Catalysis.] Ber. deut. chem. Gesell., vol. 59, B, 1926, pp. 13–36; Chem. Abs., vol. 20, 1926, p. 1164.

As an example of directive catalysis the reaction between CO and H_2 is presented, whereby a wide range of products can be obtained, depending upon the nature of the catalyst and the operating conditions.

2293. ———. [Iron Carbonyl and Carbonyl Iron.] Ztschr. angew. Chem., vol. 41, 1928, pp. 827–833; Chem. Abs., vol. 22, 1928, p. 4731.

Fe pentacarbonyl is produced on a large scale by circulating CO under pressure over sponge Fe at 150°–200° and cooling the gases evolved. It has d_4^{20} 1.453, a surface tension of 22 dynes per cm. and a viscosity of 0.0075 c. g. s. unit at 20°. Its heat of formation (liquid) is 54.2 kcal., latent heat of fusion 3.25 kcal. per mol., and heat of combustion 384.5 kcal. per mol. In alkaline solution it behaves as a powerful reducing and dechlorinating agent for organic compounds. In pentane solution it combines with Br, forming a yellow unstable compound, which rapidly decomposes with evolution of CO and formation of the reddish-brown compound, $Fe(CO)_4Br_2$. Iron pentacarbonyl decomposes at 250° in a hollow vessel heated by radiation, yielding a finely divided Fe containing about 1% C. If this is melted in a vacuum high-frequency furnace together with the requisite quantity of pure FeO, obtained by combustion of the carbonyl, an exceedingly pure Fe of high permeability, low hysteresis, and small wattage loss is obtained.

2294. ———. [Complex Catalysts.] Ztschr. Elektrochem., vol. 36, 1930, pp. 569–580; Chem. Abs., vol. 25, 1931, p. 21.

Historical review of the development of complex or mixed catalysts. Discusses reaction of CO with H_2 to give MeOH.

2294a. ———. Early Studies of Multicomponent Catalysts. Advances in Catalysis, Academic Press, Inc., New York, 1950, vol. 2, pp. 81–104.

Historical development of multicomponent catalysts is given. Their activity in NH_3 synthesis, catalytic production of H_2, hydrogenation of CO to CH_4, hydrogenation of unsaturated organic compounds, production of organic compounds by catalytic reduction of CO with H_2 under pressure, and catalytic oxidations is discussed. 52 refs. listed.

2295. Mittasch, A., and Keunecke, E. [Aluminum Oxide Activation of Iron Catalysts for Synthesis of Ammonia.] Ztschr. Elektrochem., vol. 38, 1932, pp. 666–669; Chem. Abs., vol. 26, 1932, p. 5707.

Fe catalysts containing about 10% Al_2O_3 have been prepared by different methods and their relative activities for NH_3 synthesis have been determined. Preparation of the Fe oxide–Al oxide by fusion, by coprecipitation followed by ignition in air to either 1,000° or 500°, by mixing the precipitated Fe_2O_3 with either α–or γ–Al_2O_3 and igniting to 1,100°, and by mixing γ–Al_2O_3 with precipitated Fe_2O_3 and igniting in air to 500°, all gave catalysts on reduction with H_2 that were capable of producing between 8.5 and 11.6% NH_3 at 500°, 200 atm. and space velocity of 20 l. per hr. Mixing precipitated Fe_2O_3 with α–Al_2O_3 and igniting to 500° gave a very poor catalyst. Fe prepared by the reduction of pure Fe_2O_3 gave a catalyst whose initial activity is as high as the final activity of the samples promoted with Al_2O_3; the principal function of the promoter appears, therefore, to be the prevention of crystal growth in the reduced Fe catalysts.

2296. Mittasch, A., and Kuss, E. [Ammonia Synthesis With Catalysts Derived From Complex Cyanides of Iron.] Ztschr. Elektrochem., vol. 34, 1928, pp. 159–170; Chem. Abs., vol. 22, 1928, p. 2441.

Complex cyanides of Fe or carbides derived from these cyanides are not themselves effective catalysts for the synthesis of NH_3. The active agent is elementary Fe resulting from the decomposition and reduction of the complex cyanide. The activity of the Fe may be enhanced by the presence of other materials that arise during the decomposition of the complex cyanides. The effective catalyst is then only a promoted Fe catalyst. This conclusion is supported by extensive chemical, X-ray, and magnetic studies of the complex cyanides and their decomposition products. The bearing of this research on the NH_3 catalyst patent situation in Germany is indicated.

2297. Mittasch, A., Kuss, E., and Emert, O. [Thermal Decomposition of Complex Iron Cyanides in Connection With the Ammonia Synthesis.] Ztschr. anorg. Chem., vol. 170, 1928, pp. 193–212; Chem. Abs., vol. 22, 1928, p. 2441.

Complex Fe cyanides as such are not NH_3 catalysts, but the products of their decomposition and reduction are. $(NH_4)_4Fe(CN)_6$ and $KAlFe(CN)_6$ are decomposed at high temperature in a N_2–H_2 mixture with intermediate formation of a substance corresponding in composition to $Fe(CN)_2$. The purely thermal decomposition of $Fe(CN)_2$ gives Fe, C, Fe_3C, Fe nitride and N_2, probably with the intermediate formation of FeC_2. In N_2+H_2, $Fe(CN)_2$ reacts as follows: At 230°, the C and the N in the CN groups are reduced at the same rate, and the completed reaction yields Fe. At 400° the rates of reduction differ and there is obtained, probably through the intermediate formation of FeC_2, a mixture of Fe, Fe_3C, C, and probably the 2 latter in varieties easily reduced by the N_2–H_2 mixture. These varieties are changed by prolonged heating above 400°, although the Fe_3C can still be reduced. Fe must always be formed first; Fe_3C could not be prepared under any conditions without the formation of Fe, while it is possible to control the conditions so as to obtain only Fe. The NH_3 contact catalysts prepared from complex Fe cyanides must always contain Fe and are composed chiefly or exclusively of products of reduction. These are activated by the N_2–H_2 mixture and constitute then a catalyst. Fe_3C in finely divided form is readily reduced by H_2 to a compact form, at least superficially, so that the catalytic action of Fe_3C as such has never been observed.

2298. Miyahara, S. [Theory of the Transformation of Magnetite at Low Temperatures. I.] Proc. Phys. Math. Soc. Japan, vol. 24, 1942, pp. 49–54; Chem. Abs., vol. 41, 1947, p. 6093.

Magnetic character of magnetite is discussed on the basis of the Wilson model of semiconductors and the Bloch theory of ferromagnetism. It is concluded that the transformation of magnetite at low temperatures is not caused by the change of axis of easiest magnetization but is primarily connected with the special electronic structure of this crystal.

2299. Okamura, T., and Ogawa, S. [Magnetic Behavior of Magnetite at Low Temperature. II.] Proc. Phys. Math. Soc. Japan, vol. 25, 1943, pp. 43–46; Chem. Abs., vol. 41, 1947, p. 6093.

Magnetization intensities of magnetite in 3 directions (110), (111), and (100), were measured at –195°. They are much smaller than those at 10° and different according to the directions when the magnetizing field is smaller than about 6,000 oersteds. They coincide with each other at 7,500 oersteds. Above this field strength, the low-temperature magnetization curve is a little higher than the room-temperature curve.

2300. Miyake, S. Orientations of Metallic Crystals, Formed by the Evaporation Method. I. Iron Crystals Formed on the Cleavage Plane of Zinc Blende. Proc. Phys. Soc. (Japan), vol 1, 1946, pp. 6–11; Chem. Abs., vol. 44, 1950, p. 9207.

Electron-diffraction experiment of a film of Fe crystals, formed by the evaporation method on the cleavage plane of Zn blende, was made. The orientation of the Fe crystals in the film depends upon the temperature of the Zn-blende crystal at the time of the film formation, because the temperature affects the quantity of gas molecules absorbed in the Zn-blende crystal. Heating after the formation of the Fe crystals has no effect on their orientations. The film formed at high temperatures or heated after their formation gives irrational spots or mesh pattern in the electron diffraction. This is attributed to finely repeated twins of the Fe crystals.

2301. Moehrle, E. [Production of Diesel and Fuel Oils From Coal Tar.] Tech. Mitt. Krupp, vol. 5, No. 2, 1937, pp. 38–39; Brennstoff-Chem., vol. 18, 1937, p. 305; Chem. Abs., vol. 31. 1937, p. 8875.

Process is described for separating pitch and oil from coal tar by fractional solution in gas oil at boiling temperature. A virtually asphalt-free mixture of gas oil and tar oil is obtained. Some improvement in the method has been found by substituting synthetic Kogasin for the gas oil.

Mogilevskaya, A. M. *See* abs. 360.

Mohammad, A. *See* abs. 2770.

Mohr, W. *See* abs. 1044.

2302. Moignard, L. A. and Dent, F. J. Catalytic Synthesis of Methane for Town-Gas Manufacture. Joint Research Comm., 49th Rept. Gas Research Board Pub. 20; Gas Times, vol. 47, 1946, No. 601, pp. 41–43; No. 603, pp. 40–42; No. 605, pp. 40–41.

Report of investigation of methods is given for the control of the reaction involved in the catalytic synthesis of CH_4 from H_2 and CO so that the reaction can be carried out at relatively low temperatures and at the high space velocity necessary for gas manufacture. The problems of C deposition and sintering were studied experimentally. By increasing the rate of dissipation of heat and the proportions of alumina, the deposition of C is decreased and less sintering occurs.

Moignard, L. S. *See* abs. 694.

Moise, J. E. *See* abs. 2459.

2303. Molstad, M. C., and Dodge, B. F. Zinc Oxide-Chromium Oxide Catalysts for Methanol Synthesis. Ind. Eng. Chem. vol. 27, 1935, pp. 134–140; Chem. Abs., vol. 29, 1935, p. 2313.

Mixtures of ZnO and Cr oxide, made by NH_3 precipitation from a solution of the mixed nitrates, are active, rugged MeOH catalysts. The most active mixture in a short test is $Zn_{75}Cr_{25}$, in agreement with other investigators that excess Zn is necessary. Catalysts containing more Cr increase in activity during tests, and the improvement is accelerated by temperatures up to 100° above maximum-activity temperature so that the best catalyst for long service is $Zn_{50}Cr_{50}$, which produces almost pure MeOH and is unaltered by long use at temperatures considerably above the normal operating temperature.

Momen, S. A. *See* abs. 2446.

2303a. Monceaux, P. [Controlled Oxidation of the Gas of Saint-Marcet in Air at Atmospheric Pressure.] Mém. services chim. état. (Paris), vol. 32, 1945, pp. 253–298; Chem. Abs., vol. 42, 1948, p. 4327.

Oxidation of CH_4, C_2H_6, and natural gas was studied under various conditions of temperature, ratio of air to CH_4, and rate of flow. The natural gas was 92% CH_4 with <1% C_2H_6 and 5–6% N_2. The noncatalytic oxidation of CH_4 was studied over a temperature range of 500°–900° by using gas mixtures containing 10–50 parts of CH_4 in air with flow rates from 50–300 l. per hr. In all experiments the conversion of CH_4 to HCHO did not exceed 1%. With increasing time of contact the yield passed through a maximum. The yield increased with increase of temperature, the maximum shifting to shorter contact times. <700° the most favorable composition of the gas was 20% CH_4 and 80% air, while at higher temperature it was 10% CH_4. There was, however, a rapid decrease in the quantity of O_2 present which was shown to be due to the direct oxidation of CH_4 to CO and H_2. A study of the decomposition and oxidation of HCHO was made which showed that >600° the decomposition in N_2 was extremely rapid at first and then approached complete decomposition more slowly. <600° the decomposition was much slower but still appreciable. In the presence of air the HCHO was oxidized as well as decomposed. The order of the reaction for the formation of HCHO in respect to O_2 was found to lie at 1–2. The oxidation of CH_2 yielded only slightly more HCHO than did CH_4 and slightly < the natural gas. An increase in the surface of the reaction tube, with quartz, caused a decrease in the yield of HCHO and also an increased rate of decomposition of HCHO. A surface of C increased the yield of HCHO. At temperatures < 750° the % of O_2 entering into the reaction was markedly reduced by a C surface. The catalytic action of oxides of N was caused by NO_2 and not by NO.

2304. Mond, L., Hirtz, H., and Cowap, M. D. Note on a Volatile Compound of Cobalt With Carbon Monoxide. Chem. News, vol. 98, 1908, p. 165; Chem. Abs., vol. 2, 1908, p. 3315.

Finely divided Co and CO at 150° and under 50 atm. yielded small quantities of Co carbonyl; at 200° under 100 atm. the yield was higher. The Co was prepared by converting CoC_2O_4, free from Ni and Fe, to oxide, and reducing the latter to metal with H_2 in the retort used for the production of the carbonyl. The carbonyl was obtained in large orange crystals, agreeing in composition with the formula $Co(CO)_4$. It decomposes in air to a violet substance, as yet uninvestigated, and is best preserved by sealing up in H_2 or CO. It is but slowly attacked by nonoxidizing acids but very readily by oxidizing agents, for example, $Co(CO)_4+Br_2 \rightarrow CoBr_2+4CO$. It is insoluble in N_2O but more or less soluble in CS_2, ether, naphtha, alcohol, and Ni carbonyl. If these solutions stand for some time or are warmed, decomposition sets in, D_{18} 1.827; vapor tension at 15°, 11 mm. Both of these values, however, are affected by the ease with which the carbonyl decomposes and are not to be regarded as final. In an atmosphere of CO_2, the decomposition begins at 40°–45° and is complete at 130°–135°, leaving metallic Co. The melting point is 42°–46°.

2305. ———. [Some New Metallic Carbonyls.] Ztschr. anorg. Chem., vol. 68, 1910, pp. 207–219; Jour. Chem. Soc., vol. 97, 1910, pp. 798–809; Chem. Abs., vol. 4, 1910, p. 2118.

Formation and properties of $Co(CO)_3$, $Fe(CO)_5$, $Mo(CO)_6$, and Ru carbonyl (composition unknown) are discussed. Gives table of the known carbonyls and their properties.

2306. Mond, L., Langer, C., and Quinke, F. Action of Carbon Monoxide on Nickel. Proc. Chem. Soc., vol. 86, 1890, pp. 112–113; Chem. News, vol. 62, 1890, p. 97; Jour. Soc. Chem. Ind., vol. 9, 1890, p. 808.

CO in contact with Ni at temperatures 350°–450° was found to decompose, a compound of C and Ni being formed. It was identified as Ni carbonyl $Ni(CO)_4$. Similar experiments with other metals, such as Co, Fe, Cu, and Pt, gave negative results.

2307. Mond, R. L. [Metal Carbonyls.] Chim. et ind., vol. 21, 1929, pp. 681–700, 937–940; Jour. Soc. Chem. Ind., vol. 49, 1930, pp. 271–278T; Chem. Abs., vol. 23, 1929, p. 4417.

Address reviewing the preparation, properties, and applications of metallic carbonyls, with a bibliography of 91 literature refs. and 69 patents.

2308. Mond, R. L., and Wallis, A. E. Researches on the Metallic Carbonyls. Jour. Chem. Soc., vol. 121, 1922, pp. 29–32; Chem. Abs., vol. 16, 1922, p. 2457.

Composition of Mo carbonyl, redetermined by 2 methods, corresponds to $Mo_3(CO)_{26}$. It is insoluble in the common solvents. 2 yr. were required to prepare 170 mg. Ru gives 2 carbonyls, one volatile is crystalline and soluble in C_6H_6, and the other is nonvolatile, amorphous, and insoluble in C_6H_6, but soluble in C_2H_5OH and in H_2O. The formula of the latter appears to be $Ru(CO)_2$. Optimum conditions are described for the preparation of $Fe(CO)_5$. $Ni(CO)_4$, air, and moist CO heated at 200° react to give a yellow deposit, which is shown to be a colloidal basic Ni carbonate of varying composition.

Monroe, G. S. *See* abs. **1579, 1579a.**

Montgomery, C. W. *See* abs. **117, 3599.**

2309. Montgomery, C. W., and Weinberger, E. B. Product Distribution in the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Jour. Chem. Phys., vol. 16, 1948, pp. 424–425; Chem. Abs., vol. 42, 1948, p. 4437.

It is pointed out that thermodynamic equilibrium among the n-paraffins yields a distribution that is qualitatively similar to that observed experimentally. Comprises general viewpoint set forth by Craxford. that product distribution is a result of some polymerization-depolymerization equilibrium in the last stages of the process and probably involves paraffin hydrocarbons.

2310. Montgomery, C. W., Weinberger, E. B., and Hoffman, D. S. Thermodynamics and Stoichiometry of Synthesis Gas Production by the Partial Oxidation of Methane. Ind. Eng. Chem., vol. 40, 1938, pp. 601–607; Chem. Abs., vol. 42, 1948, p. 4329.

In considering the economics of Fischer-Tropsch synthesis gas production by the partial oxidation of CH_4, situations may arise where either the cost of O_2 or the cost of CH_4 may be of controlling importance. This paper presents a treatment of the thermodynamics of the CH_4–H_2O–H_2–CO–CO_2–C system, which has been extended to cover solutions of 2 maximum problems not ordinarily dealt with; namely, determination of the conditions of temperature, pressure, and $O_2:CH_4$ ratio for maximum yield of synthesis gas per mol. of O_2 and per mol. of CH_4. The numerical calculations have been made with the assumption of isothermal equilibration so that the results are of more value as standards for comparison with actual synthesis-gas units rather than as a basis for the design of such units. The calculations show that the maximum yield of synthesis gas per mol. of CH_4 or O_2 is favored at high temperatures and low pressures. In addition, the conditions of temperature, pressure, and $O_2:CH_4$ ratio necessary to prevent the formation of unburned C is given. It also is shown that the numerical calculations are much simplified if the $H_2:CO$ ratio is taken as the independent variable rather than the $O_2:CH_4$ ratio. The calculations serve to illustrate the general desirability of effecting equilibration of the combustion gases at high temperatures and low pressures. Relatively long residence time of the gases in contact with catalytic materials at lower temperatures, such as might be encountered in a reactor having a long dropping temperature gradient might be expected to cause deviations from the theoretical compositions. The magnitude of these deviations from the calculated values may be taken as a measure of the extent of re-equilibration occurring. The calculations also show that the point of maximum yield per mol. of CH_4 always requires a higher $O_2:CH_4$ ratio than the point of maximum yield per mol. of O_2. In the preferred high-temperature–low-pressure range, however, these maxima approach each other. The problem of calculating maximum yield per unit cost of reactants is, thus, very much simplified.

Moore, G. E. *See* abs. **1729.**

2311. Moore, H. Liquid Fuels and Organic Chemicals From Coal and Home-Refined Petroleum. Gas Jour., vol. 243, 1944, pp. 149–150, 155, 180, 183, 213–214; Gas World, vol. 120, 1944, pp. 166–172, 191–199; Jour. Inst. Fuel, vol. 17, 1944, pp. 65–74, 102–104; Petrol. Times, 1944, pp. 67–68, 70, 79–81, 83–84, 86; Chem. Abs., vol. 38, 1944, pp. 1861, 2469, 6066.

Reviews methods for producing liquid fuels and organic chemicals in use during 1938 and suggests outline of policy to be followed for their production in Great Britain after the war. By increasing the demand for gas, the materials for production of more liquid fuels and chemicals will become available.

2312. Moore, W. J. Parabolic Oxidation Rates of Metals. Jour. Chem. Phys., vol. 18, 1950, p. 231; Chem. Abs., vol. 44, 1950, p. 5686.

Constants, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta F^{\ddagger}$, of the transition-state theory (abs. **1283**) for the oxidation of Al, Fe, Zr, Ti, Ni, Cu, Co, Zn, and Be are compared. Except for Be, there is little variation in the $\Delta F^{\ddagger}$ values; hence reactions with high $\Delta H^{\ddagger}$ also have high $\Delta S^{\ddagger}$. A schematic diagram of the potential-energy barriers for vacancy formation and diffusion shows that, for equal diffusion barriers, the higher the heat of adsorption, the lower the effective $\Delta H^{\ddagger}$. Since a high heat of adsorption implies an immobile adsorbed film, it may also be associated with a large negative ΔS of adsorption; this may help explain the approximate constancy of $\Delta F^{\ddagger}$.

Morcom, A. R. *See* abs. **1629.**

Moreau, J. *See* abs. **190.**

2313. Morgan, G. T. Organic Syntheses Facilitated by Pressure. Chem. and Ind., vol. 50, 1931, pp. 104–109; Chem. Abs., vol. 25, 1931, p. 1809.

Review with many references to the patent literature of important syntheses facilitated by pressure. Among the reactions discussed are the formation of hydrocarbons, alcohols, aldehydes, ketones, etc., by pressure reactions in the gas phase from CO and H_2 with various catalysts.

2314. ———. [Synthesis of Aliphatic Compounds Under Pressure.] Bull. soc. chim. Belg., vol. 45, 1936, pp. 287–312; British Chem. Abs., 1936, A, p. 1090.

Review. At 400° per 200 atm. using $CoSO_4$ with some CuO and MnO as catalyst, CO_2 and H_2 gave a mixture containing MeOH (17%), EtOH (22%), higher alcohols, chiefly normal (11%), and CH_4 (47%). Other reactions are reviewed.

2315. Morgan, G. T., and Bone, W. A. Discussion on Catalytic Reactions at High Pressures. Proc. Roy. Soc., London, vol. 127, A, 1930, pp. 240–267; British Chem. Abs., 1930, A, p. 867.

Work on the NH_3 synthesis and on the synthesis of MeOH from CO and H_2 is briefly and historically reviewed. The aldolization hypothesis, which accounts for the formation of higher aldehydes and alcohols in the latter synthesis, is discussed. Work in the high pressure gas research laboratories at the Imperial College during the last 3 yr. is reviewed with special reference to the formation of formaldehyde, MeOH, and CH_4 from CO and H_2. By selecting a suitable catalyst and temperature, any one of these 3 substances may be produced to the practical exclusion of the other 2. The absence of satisfactory equilibrium data in regard to the MeOH synthesis previous to the present series of investigations is pointed out, and the extreme importance of determining the equilibrium constant by approaching the equilibrium from both sides is emphasized. Discusses errors due to the fact that at the high pressures used the equilibrium mixtures do not obey the simple gas laws.

2316. Morgan, G. T., and Taylor, R. Ethyl Alcohol, a Product of High-Pressure Synthesis. Nature, vol. 125, 1930, p. 889; Proc. Roy. Soc. (London), vol. 131, A, 1931, pp. 533–540; British Chem. Abs., 1931, B, p. 833; Chem. Abs., vol. 24, 1930, p. 3985.

This alcohol has been obtained by Morgan and Taylor with various catalysts from CO and H_2.

2317. ———. Ethyl Alcohol, a Product of High-Pressure Synthesis. Proc. Roy. Soc., London, vol. 131, 1931, A, pp. 533–540; Chem. Abs., vol. 25, 1931, p. 4521.

Seven different catalysts, the composition of which is given, were found to give appreciable quantities of EtOH. 1 of these catalysts, prepared from Co nitrate and Zn permanganate with an addition of clay, contained after use: ZnO. 7.9; MnO, 26.34; Co, 29.9; K_2O, $+Na_2O$, 7.4; SiO_2, 8.8; Al_2O_3, 2.5; CaO, 0.4; Fe, 0.3; and C, 8.9%. The gas mixture contained $H_2:CO::2:1$. The pressure was 200 atm. and temp. was 380°–410° C. In these circumstances, EtOH was found to account for 9.8% of the total CO converted. Other products were: Other alcohols, 25.5; acids, 7.4; acetaldehydes, 5.3; and CH_4, 50.0%.

2318. Morgan, G. T., Hardy, D. V. N., and Proctor, R. A. Methanol Condensation as Modified by Alkalized Catalysts. Jour. Soc. Chem. Ind. (London), vol. 51, T, 1932, pp. 1–7; British Chem. Abs., 1932, B, p. 250; Chem. Abs., vol. 26, 1932, p. 4792.

Cr and Mn oxide catalysts in molecular proportions gave higher yields of higher alcohols and lower yields of MeOH in the MeOH synthesis from CO and H_2 when precipitated by alkali hydroxides than when formed by ignition of the nitrates. The catalyst impregnated with 9.8% Rb gave the highest yield of higher alcohols. Theories to account for this effect are discussed. A careful analysis was made of the product obtained by using a Cr–Mn catalyst containing 15% Rb.

2319. Morgan, G. T., Taylor, R., and Hedley, T. J. Synthesis Under High Pressure. Interaction of Carbon Monoxide and Hydrogen. Jour. Soc. Chem. Ind., vol. 47, 1928, pp. 117–122T; Chem. Abs., vol. 22, 1928, p. 2919.

Chemical Research Laboratory at Teddington, devoted to general investigations of high-pressure synthesis, is described in detail. Numerous illustrations and drawings of high-pressure equipment are reproduced. A Tantiron apparatus for generating CO from HCO_2H and H_2SO_4 is described. MeOH has been synthesized at 400 atm. in relatively large quantities by circulation of CO–H_2 mixtures over any one of several catalysts made by mixing ZnO with other metallic oxides. Other ZnO catalysts containing alkaline substances were used to synthesize mixtures of MeOH and higher alcohols. These mixtures invariably contained small quantities of aldehydes, acids, and esters. It was observed that primary alcohols only were identified; the aldehydes formed corresponded to the alcohols; addition of Co to the basic Zn chromate catalyst favored the production of higher alcohols; rise in temperature of the catalyst favored MeOH formation. The reactions are assumed to involve primary HCHO synthesis. The results so far obtained on the MeOH equilibrium are in agreement with Audibert and Reineau's equation: $\log K_p = P_{MeOH}/P_{CO}\cdot(P_{H_2})^2 = 27{,}000/(4.517T) - 3.5 \log T - 3.6$.

2320. Morgan, G. T., and others. Application of High Pressure in the Synthesis of Organic Compounds. Trans. World Power Conf., 3d Conf., London, June 1936, Chem. Eng. Cong., 22 pp.

Work at Chemical Research Laboratory, Teddington, since 1926 is summarized.

Mori, I. *See* abs. **3173.**

Morikawa, K. *See* abs. **3606, 3607, 3608, 3609, 3610, 3611.**

2321. Morikawa, K., Benedict, W. S., and Taylor, H. S. Activity of Specific Bonds in Complex Molecules at Catalytic Surfaces. I. The Carbon-Hydrogen Bond in Methane and Methane-d_4. Jour. Am. Chem. Soc., vol. 58, 1936, pp. 1445–1449; Chem. Abs., vol. 30, 1936, p. 6632.

CH_4 undergoes exchange with D_2, CD_4, and D_2O on active Ni catalysts at 138° and above. At 184° the rate of reaction decreases in the order CD_4, D_2, and D_2O. The activation energy of reaction for CD_4 is approximately 19 kg.-cal., and for D_2 approximately 28 kg.-cal. The reaction is explained by an activated, dissociative absorption of CH_4 on surface areas not occupied by H–D or D_2O.

2322. ———. Activation of Specific Bonds in Complex Molecules at Catalytic Surfaces. II. Carbon–Hydrogen and Carbon–Carbon Bonds in Ethane and Ethane-*d*. Jour. Am. Chem. Soc., vol. 58, 1936, pp. 1795–1800; Chem. Abs., vol. 30, 1936, p. 7435.

C_2H_6 and D_2, heated in contact with a Ni catalyst, undergo an exchange reaction at 100°–130°, and yield mixed methanes at 160°–300°. The CH_4 reaction was followed by measuring the infrared absorption and by volume changes in the gas mixture. H_2 is preferentially adsorbed on the catalyst and tends to inhibit CH_4 formation. At low H_2 concentrations, the side reactions $2C_2H_6 \rightarrow C + 3CH_4$ and $C + 2H_2 \rightarrow CH_4$ become predominant. The activation energy of formation of CH_4 from C_2H_6 and H_2 is approximately 43 kg.-cal., and that of CD_4 is approximately 5 kg.-cal. higher. These reactions are explained in terms of a dissociative adsorption theory. More energy is required to activate the C–C bond than the C–H bond. C_2D_6 was prepared by 2 treatments of C_2H_6 with pure D_2 at 138° for 2–3 hr.

Morita, K. *See* abs. **1681, 1682.**

Morlet, E. *See* abs. **2094a.**

2323. Morley, R. J. Winkler Generators for Manufacture of Water Gas. BIOS Final Rept. 333, 1945, 37 pp., PB 25,587; TOM Reel 227.

All the available information concerning Winkler generators, contained in CIOS reports and in documents brought back from Germany in 1945 is collected and combined with literature references to give a comprehensive account of the history and present status of the process. The process is technically sound, and it is possible to operate Winkler generators on bituminous coals, low-temperature coke from bituminous coal or even anthracite; operation, however, is not satisfactory, and, in general, it appears that the process is not economic for such fuels, where cheap fuel and coke-oven water-gas generators are available. The Winkler process is not suited to making town's gas, as the calorific value is low, and its field of application appears to be limited to the large scale production of water gas, to be used for manufacture of H_2, MeOH, or Fischer-Tropsch synthesis gas, of producer gas to be used as a fuel or power gas, and of NH_3 synthesis gas, but, in all cases, based on a cheap fuel. The 2 great disadvantages of the Winkler process are its relatively poor thermal efficiency (66 and 60%, respectively, for water-gas and power-gas production at Leuna; the thermal efficiency is raised somewhat if all the C in the escaping dust is recovered for boiler fuel) and the cost of O_2. A further disadvantage of O_2-gasification is that any O_2 added must eventually appear as CO_2 in the synthesis gas, hence greater compression and water scrubbing costs are incurred to remove it with corresponding capital costs. The capital cost of a Wrinkler plant, including O_2 plant, waste heat boilers, etc., is somewhat greater than that of a corresponding coke water-gas plant, including coke ovens. The O_2 plant probably costs more than the Winkler plant it supplies. A rough figure for labor costs of water gas may be taken as 0.4 man-hr. per 1,000 m.^{3} of synthesis gas. Maintenance costs at Leuna averaged in 1935 RM 1.75 per 1,000 m.^{3} for an output of 20,000 m.^{3} per hr. of synthesis gas; for power gas RM 0.46 per 1,000 m.^{3} for an output of 50,000 m.^{3} per hr. Extensive data are given for plant operation and performance for production of both water and power gas from grude-coke and brown coal.

2324. ———. Wintershall-Schmalfeldt Process for the Manufacture of Synthesis Gas at Lutzkendorf. BIOS Final Rept. 1142, 1947, 33 pp., PB 78,242.

Detailed description of the process with figures and flow sheets. The process consists essentially of gasification of dry brown-coal dust in the entrained state. The heat of reaction is supplied by burning producer gas in 1 of 2 regenerators, used alternately, the heat being stored in checker brick and then given up to a mixture of recycled synthesis gas and steam. Heat also had been supplied by burning O_2 in the recycled gases. The producer gas is made by gasifying dried brown-coal dust entrained in the recycled gas and steam, heated to over 1,000°, while passing up and down 2 large generators in series. The sensible heat in the final gases was used to dry and disintegrate the raw brown coal. The process is now technically established, but dust losses are high, and synthesis gas contains organic S-ring compounds and gum-forming compounds deleterious to the Fischer-Tropsch catalyst, although not to the hydrogenation of oil and tar. It is reported that active C had been used in the purification train to remove these undesirable impurities and with considerable success. The plant is very large for the output, and capital costs are high, probably three times that of the Winkler plant. In its present state of development, the process appears to be less economic than the Winkler process, operating under similar circumstances. The operating cost per 1,000 m.^{3} of synthesis gas is calculated at RM 27.4 and RM 22.9, respectively. Additional costs, which should be debited to the Schmalfeldt process, have to cover the cost of disposal of the large amounts of muddy effluent, that of the higher inert content of water gas (6% as against 3% in Winkler gas), and the extra purification if the gas is used for the Fischer-Tropsch synthesis.

———. I. G. Farbenindustrie A.-G. Works at Leuna. III. Methanol and Higher Alcohol Synthesis. *See* abs. 1476.

2325. Morozov, N. M. Kinetics of Sorption Processes of Hydrogen on Iron. Trans. Faraday Soc., vol. 31, 1935, pp. 659–668; Chem. Abs., vol. 29, 1935, p. 4233.

In the temperature range −190°–400°, the sorption of H_2 on pure Fe (reduced from precipitated Fe_2O_3) occurs as 3 types: Van der Waals adsorption, activated adsorption, and activated diffusion. In certain temperature ranges, it is possible to separate these processes and investigate the kinetics of each. Heats of activation are approximately 20,000 kg.-cal. for activated adsorption and 8,000 kg.-cal. for activated diffusion. Between 300° and 400°, the activated adsorption is instantaneous and entirely reversible; this permits the calculation of heats of adsorption, which, for 1.0, 1.25, and 1.50 cc. of H_2 adsorbed on 24 gm. of Fe, are, respectively: 9,220, 6,820, and 6,140 cal. per mol. Activated adsorption diminishes van der Waals adsorption, although under certain experimental conditions the absence of such relation was found.

———. *See* abs. 1653.

2325a. Morrell, C. E., Carlson, C. S., McAteer, J. H., Robey, R. F., and Smith, P. V. Products From Hydrocarbon Synthesis. Am. Chem. Soc., 121st Meeting Abs., March–April 1952, p. 19–I.

Reaction of CO and H_2 over promoted Fe catalysts produces a valuable mixture of hydrocarbons and oxygenated organic chemicals. On a molal basis, CH_4 is obtained in greatest yield with progressively lower yields of hydrocarbons of increasing molecular weights. Yields of 2–C oxygenated compounds, including acetaldehyde. Ethanol and acetic acid are greater than those of both higher and low number of C atoms. Yields of higher molecular weight compounds decrease progressively with increasing molecular weight. Approximately 10 wt. % oxygenated organic compounds is obtained in the H_2O phase, including alcohols containing 1–5, aldehydes 2–5, ketones 3–6, esters 3–6, and acids 1–4 C atoms. The alcohols are predominately normal, primary alcohols, but up to 20 wt. % of the alcohols are secondary, tertiary, and branched chain primary alcohols. For the separation and purification of these H_2O-soluble chemicals, fractional distillation alone is not enough, but H_2O extractive distillation or extractive distillation with polar and nonpolar type organic solvents can be used. Caustic extraction and hydrogenation may be used to simplify the recovery problem. Approximately 20 wt. % oxygenated organic compounds are obtained in the oil phase, including alcohols containing 1–14, aldehydes and ketones 2–14, acids 2–14 and esters 3–20 or more C atoms. The molal yields of alcohols, carbonyls and acids are a maximum at 3, 2 and 5 C atom compounds, respectively. Alcohols have been isolated from narrow boiling fractions of synthesis oils by formation of nonvolatile esters with boric acid or phthalic anhydride. Extraction with hot H_2O removes acids and alcohols from the oil. Room temperature extraction with aqueous MeOH is effective in removing oxygenated compounds of all types from synthesis oils.

Morrell, J. C. *See* abs. 204, 776.

2326. Morrell, J. C., and Egloff, G. Many Future Sources of Motor Fuel. Oil Gas Jour., vol. 26, No. 18, 1927, pp. 202, 400, 402, 404; Chem. Abs., vol. 22, 1928, p. 152.

Summary of the present status of motor fuel manufacture with a discussion of probable future developments. Starting with crude petroleum, the other sources are taken up with a brief explanation of the manufacturing necessary to convert raw material into fuels. The Fischer-Tropsch and the Bergius processes are described briefly and their commercial possibilities pointed out.

2327. Morris, H., and Selwood, P. W. Magnetic Moments on Some Catalytically Active Substances. Jour. Am. Chem. Soc., vol. 65, 1943, pp. 2245–2252; Chem. Abs., vol. 38, 1944, p. 294.

Directions for making magnetic-susceptibility measurements; significance of such measurements is pointed out in the determination of the ferromagnetism of a catalyst and its effect upon the activity.

Morris, H. E. *See* abs. 301, 302.

2328. Morris, V. N., and Reyerson, L. H. Qualitative Study of the Catalytic Hydrogenation of the Oxides of Carbon. Proc. Indiana Acad. Sci., vol. 36, 1927, pp. 203–206; Chem. Abs., vol. 22, 1928, p. 345.

Attempts were made to synthesize HCHO and MeOH at atmospheric pressure. The most favorable results for HCHO were obtained when using a platinized gel as catalyst with mixtures of H_2 and CO_2. With H_2, CO, and a Cu catalyst the result appeared to be a mixture of the products. Pressures varying 8–27 atm. gave no better results than 1 atm. for these syntheses.

Morrison, J. L. *See* abs. 2409.

Moulin, J. *See* abs. 2721.

2329. Mourev, H., Chovin, P., and Garcin, M. [Utilization of Methane.] Ann. mines et carburants, No. 4, 1944; Génie civil, vol. 122, June 15, 1945, p. 95; Fuel Abs., vol. 2, No. 5010, November 1945.

Discusses modern industrial processes using CH_4 as raw material including pyrolysis to give C-black, H_2, C_2H_2, C_2H_4, etc., conversion to HCHO and MeOH, and synthesis gas for the Fischer-Tropsch process.

2330. Movius, H. G., and Scott, H. Similarity of the Magnetic Change in Cementite and Ferrite. Chem. Met. Eng., vol. 22, 1920, pp. 1069–1070; Chem. Abs., vol. 14, 1920, p. 2327.

Thermal curves were taken by the inverse rate method. The materials studied were a pure Fe, a eutectoid C steel, and a 1.94 C Fe–C alloy containing 0.1% Si and 0.005% S.

2331. Moynot, H. [Adaptation of Fuels to Modern Diesel Engines.] Sci. et ind., Tech. ind. pétrole, 1939, No. 284, pp. 88–94; Chem. Abs., vol. 33, 1939, p. 7520.

Discusses combustion of fuels in diesel engines. Gives suggested specifications for diesel fuels. Fischer-Tropsch gas oils have higher calorific values than normal gas oils, the values of which are very similar and seldom determine.

Muchlinski, A. *See* abs. 3578.

Mueller, A. C. *See* abs. 2441, 2442.

Mühlbert, H. *See* abs. 1650.

2332. Muhlert, F. [Franz Fischer's Synthesis of Benzines.] Apparatebau, vol. 38, 1926, pp. 143–144; Chem. Abs., vol. 20, 1926, p. 2743.

2333. ———. [Fuels and Combustible Liquids. Recent Developments in Germany.] Chaleur et ind., vol. 15, 1934, pp. 229–234; Chem. Abs., vol. 29, 1935, p. 907.

General literature review of recent progress in Germany on the treatment of coal for the production of gaseous and liquid products.

2334. ———. [Production of Synthesis Fuels and Oils in England.] Chaleur et ind., vol. 17, 1936, pp. 119–123; Chem. Abs., vol. 30, 1936, p. 5389.

Describes Bergius and Fischer-Tropsch processes, and points out their economic value.

2335. ———. [Growth of Synthetic Liquid Hydrocarbon Industries in Germany.] Chaleur et ind., vol. 20, 1939, pp. 355–360; Chem. Abs., vol. 33, 1939, p. 6019.

Review of development of processes for synthesis of liquid hydrocarbons from bituminous and brown coals. Illustrated description of Fischer-Tropsch Ruhrchemie plant.

2335a. Mulford, R. N. R., and Russell, W. W. Catalytic Hydrogenation of the Oxides of Carbon to Higher Hydrocarbons. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 1,969–1,974.

The effects of carbonate, chloride, sulfate, thiosulfate, and sulfide, added singly as K or Na salts prior to catalyst precipitation, upon Ce-promoted, Cu-containing Co catalysts in the synthesis of hydrocarbons from the oxides of C at atmospheric pressure have been studied. All of these Co catalysts produced oil when the initial CO_2–H_2 mixture was first passed over a supported Fe, water gas catalyst, but with no water gas catalyst present only the Co catalysts containing K_2CO_3 or K_2SO_4 produced oil. In general the effects of certain of these catalyst additives were to alter the distribution between liquid and gaseous synthesis products, to increase oil yields, and to shift the temperature range of maximum oil yields. The effects of the additives are attributed to selective activation and/or beneficial poisoning of the Co catalysts.

Müller, A. *See* abs. 3674.

2336. Müller, E. R., and Kallenberg, S. [Production of Petroleum Hydrocarbons From Carbon Monoxide and Hydrogen at Ordinary Pressure.] Ing. Vetenskaps Akad. Handl., No. 106, 1930, 39 pp.; Brennstoff-Chem., vol. 12, 1931, p. 215; Chem. Abs., vol. 26, 1932, p. 2302.

Description of the application of the Fischer-Tropsch process. Pine charcoal was gasified with steam giving 1 m.^{3} water gas from 300–400 gm. charcoal. This was treated in an electrically heated converter consisting of an upright Cu cylinder with 7 catalyst tubes 20 x 300 mm. Efficient catalysts were Co–Fe–Zn (2.5:1:2) and Co–Fe–Zn–Cu (2.5:1:1:1) precipitated from the nitrates with soda, washed with water, dried and reduced at 350° with H_2. In this apparatus, with 3,000 cc. of catalyst and a temperature 270°–290°, 800 l. of water gas produced in 21 hr. 55 gm. of liquid and solid hydrocarbons (70 gm. per m.^{3} water gas). The benzine boiled 90% below 180°, the oil 70% below 250°.

2337. Müller, F. [Low-Temperature Carbonization of Coal in Conjunction With the Fischer-Tropsch Hydrocarbon-Synthesis Process.] Tech. Mitt. Krupp, Tech. Ber., vol. 6, 1938, pp. 47–49; Brennstoff-Chem., vol. 20, 1939, pp. 141–144; Chem. Abs., vol. 33, 1939, pp. 6025, 9590.

It was previously pointed out that, by using low-temperature coke for water-gas production for the Fischer-Tropsch process instead of high-temperature coke, a maximum oil yield would be attained. When using low-temperature tar as fuel oil, the importance of mixing it with other oils is not as great as was formerly assumed. Moreover, low-temperature tar can be used directly as fuel oil. The low-temperature carbonization of coal in combination with the Fischer-Tropsch process is particularly suitable where coke ovens are not available and gas production is not of interest. In this way, the yield of clean oil amounts to 20–30% more than with high-temperature carbonization. Moreover, because of the specifically better usefulness of low-temperature coke for the water-gas process, a saving of coal is obvious. It is immaterial whether gas coal or flame coal is used, since both of them will yield an appropriate coke in indirectly heated ovens. Moreover, the water gas made from low-temperature coke more nearly meets the specified composition for synthesis gas—a CO:H_2 ratio of 1:2—the water gas from high-temperature coke showing a ratio of 1:1.25 and that from low-temperature coke 1:1.15–1.6.

2338. ———. [Hard-Coal Processing Development.] Glückauf, vol. 75, No. 33, 1939, pp. 706–711; Coke Smokeless-Fuel Age, vol. 2, 1940, p. 70.

Paper presented before the Verein bergbaulichen Interessen discusses the technology and operation of the German byproduct coking industry combined with the production of metallurgical coke, the low-temperature carbonization of hard coal and the production of semicoke, the preparation of coal for coking and chemical treatment, the liquefaction of coal, and the advantages of the Fischer-Tropsch process for producing a wide range of synthetic products from coal, coke, semicoke, or coke-oven gas. It is emphasized that best results are secured by combining the process with low-temperature rather than high-temperature carbonization of hard coal.

Müller, H. Generation of Water Gas From Brown Coal in the Pintsch-Hillebrand Generator of the Hamburg Gas Works. II. *See* abs. 3277.

Müller, J. *See* abs. 3052, 3053.

2339. Müller, W. J., and Graf, E. [Theory of the Generator and Water-Gas Processes.] Brennstoff-Chem., vol. 20, 1939, pp. 241–246; Chem. Abs., vol. 34, 1940, p. 3904.

Attempt to follow the processes quantitatively on a kinetic basis.

2340. **Müllin, C. E.** Higher Fatty Alcohols. Soap Sanit. Chemicals, vol. 14, No. 12, 1938, pp. 27–29, 69; Chem. Abs., vol. 33, 1939, p. 1263.

Several methods for the production of higher aliphatic alcohols are discussed briefly among which is the direct catalytic synthesis from H_2 and CO.

Multer, H. J. *See* abs. 202.

Munderloh, H. *See* abs. 1124.

2341. **Mungen, R., and Kratzer, M. B.** Partial Combustion of Methane With Oxygen. Ind. Eng. Chem., vol. 43, 1951, pp. 2782–2787.

Partial combustion of CH_4 with O_2 at 300 p. s. i. g. has been studied on a pilot-plant scale. The independent variables given primary attention were the $O_2:C$ feed ratio, the preheat temperatures of the feed streams, and the space velocity. The reaction is assumed to proceed in 2 steps—a primary reaction when CO_2 and H_2O are the main products of the reaction of CH_4 and O_2 followed by reforming of CH_4 with CO_2 and H_2O to CO and H_2. The reforming reaction appears to be the rate-controlling step in the process. Equilibrium was not attained under the conditions employed. The calculated final reaction temperatures ranged from 2,000°–2,500° F. The partial combustion of CH_4 with O_2 under assumed commercial conditions was shown to be a practical method of supplying feed gas to the hydrocarbon synthesis process.

Murakami, T. *See* abs. 1483.

2342. **Muraour, —.** [Manufacture of Liquid Fuels From Coal.] Recherches et inventions, vol. 6, 1925, pp. 390–392; Chem. Abs., vol. 19, 1925, p. 1487.

Brief outline of the results obtained in Germany by application of the following processes: Low-temperature carbonization; manufacture of Synthol; manufacture of MeOH from water gas; direct hydrogenation of coal.

Murata, K. *See* abs. 2500a.

2343. **Murata, Y.** Synthesis of Solid Paraffins From Carbon Monoxide and Hydrogen. Chem. Rev. (Japan), vol. 7, 1941, pp. 352–370; Chem. Abs., vol. 35, 1941, p. 8251.

Review with over 70 refs.

———. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXII. Composition of Gases and Flow Velocity. *See* abs. 1906.

———. *See* abs. 1859, 1860, 1861, 1862, 1863, 1864, 1865, 1868, 1872, 1875, 1876, 1877, 1882, 1883, 1889, 1905, 3468.

Murata, Y., and Hara, I. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXIV. Influence of Water Vapor on Iron Catalysts. *See* abs. 1906b.

Murata, Y., and Makino, S. Benzine Synthesis From Carbon Monoxide and Hydrogen. LII. Influence of the Initial Materials, Carriers, and Filling Agents Upon the Iron Catalyst. *See* abs. 1888.

Murata, Y., and Tsuneoka, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXX. Influence of Catalyst Concentration. *See* abs. 1866.

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXIII. Relation of Free Space in the Reaction Tube and the Reaction Rate of the Initial Gas, and Also the Influence of Materials Mixed With the Catalyst. *See* abs. 1869.

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXVIII. Relation Between Conditions of Synthesis and the Unsaturation of the Benzine Produced. *See* abs. 1874.

Murata, Y., and Yamada, T. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. LIV. Influence of Carbon Dioxide in the Initial Gas Upon the Iron Catalyst. *See* abs. 1890.

———. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. LV. Influence of Nitrogen, Methane, Oxygen, and Ammonia in the Initial Gas Upon the Iron Catalyst. *See* abs. 1891.

Murata, Y., and Yasuda, M. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LIX. Activation of Iron-Copper Catalysts by Boron. *See* abs. 1895.

Murata, Y., Ishikawa, S., and Tsuneoka, S. Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressure. XXXI. Influence of Current Velocity. *See* abs. 1867.

Murata, Y., Makino, S., and Tsuneoka, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLVIII. Influence of Addition of Copper and Alkali on New Iron Catalysts. *See* abs. 1884.

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen at Ordinary Pressure. XLIX. Influence of Various Metals, Metal Oxides and Precipitants on Iron-Copper-Kieselguhr Catalysts. *See* abs. 1885.

Murata, Y., Matsumoto, E., and Hoshino, S. Gasoline Synthesis From Carbon Monoxide and Hydrogen. LXXIII. Action of Carbon Monoxide on Iron Catalysts. *See* abs. 1906a.

Murata, Y., Sawada, Y., and Takezaki, Y. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LVIII. Mutual Influence of Boric Acid and Alkali in Promoting Activities of Iron-Copper Catalysts. *See* abs. 1894.

Murata, Y., Yashiro, R., and Tashiro, E. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LX. Effect of Copper on Iron Catalysts. *See* abs. 1896.

Murata, Y., Nakagawa, M., Tashiro, E., and Umemura, T. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXIV. Methods of Preparing Iron Catalysts. *See* abs. 1900.

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXV. Reduction by Hydrogen and Heat Treatment of Iron Catalysts. *See* abs. 1901.

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXVI. Reduction of Iron Catalysts. *See* abs. 1902.

Murata, Y., Tatsuki, Y., Yamada, H., and Sawada, Y. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LVII. Effect of Some Added Substances on Iron-Copper Catalysts. *See* abs. 1893.

Murata, Y., Yoshioka, Y., Oji, G., and Saito, S. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXI. Reaction Temperature and Durability of Iron Catalysts. *See* abs. 1897.

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXII. Durability of Iron Catalyst and the Composition of Gas Used in the Synthesis. *See* abs. 1898.

———. Synthesis of Benzine From Carbon Monoxide and Hydrogen. LXIII. Iron Catalysts and the Composition of Gas Used in the Synthesis. *See* abs. 1899.

2344. **Murphree, E. V.** Research and Development in the Oil Industry. Petrol. Refiner, vol. 25, No. 10, 1946, pp. 161–162.

The use of natural gas and coal as raw materials for gasoline in competition with crude oil is discussed and emphasis is put upon the application of the fluidized catalyst to the Fischer-Tropsch process. The importance of using the fluidized catalyst is made evident by the great reduction possible in the number of reactors required for an equivalent production of liquid fuel. For a plant to produce 10,000 bbl./day of synthetic hydrocarbons, using the German plant design, 128 reactors would be required having a cooling surface of 5,800,000 sq. ft. By using a fluidized catalyst, it is possible to reduce the number of reactors to 4 and the total cooling surface to 250,000 sq. ft. This means a great reduction in investment costs as well as a considerable decrease in maintenance and operating costs. This use of catalyst in fluidized form in the Fischer-Tropsch synthesis is one of the outstanding advances in the oil industry. Improvements also have been made in methods of producing synthesis gas. One process being considered commercially for both natural gas and coal involves partial combustion with O_2 to produce the $CO-H_2$ gas mixture required. In the case of coal, steam is used along with the O_2. From an economic standpoint, production of liquid products from natural gas using a modified Fischer-Tropsch operation appears reasonably attractive. The cost of producing gasoline may be slightly lower than the cost of production of gasoline from crude oil. There is, however, a substantially higher investment involved in the production from natural gas. A plant to produce about 9,000 bbl./day of gasoline along with 1,800 bbl. of gasol from coal, using the fluidized technique, is estimated to cost $42,000,000. In addition to the gasol and gasoline produced, about 40,000,000 cut. ft. of gas/day of 1,000 B. t. u. would be produced. Crediting this at $0.25/1,000 cu. ft. and the gasol and certain chemicals at a suitable figure, then the cost of gasoline based on coal at $2.50/ton comes roughly to $0.0725/gal., a cost not greatly exceeding that of a similar grade gasoline from crude oil at present crude prices.

2345. ———. Natural Gas, Coal, Oil Shale as Sources of Liquid Fuels. Oil Gas Jour., vol. 46, No. 49, 1948, pp. 66, 68–70, 95–96.

1. Statement to the Committee on Interstate and Foreign Commerce on the House of Representatives Bill 5475 dated March 5, 1948. Resources of crude oil and raw materials for synthetic liquid fuels production in the United States are outlined, and brief descriptions are given of processing methods. Preliminary figures are given on possible costs and material requirements for production of synthetic fuels from natural gas, coal, and oil shale in comparison with petroleum.

Approximate investments and steel requirements for maximum gasoline production

Plant location	Gulf coast		Western Pa.	Colo.-Calif.[1]
Product market area	Eastern seaboard			Calif.
Raw material	Crude oil	Natural gas	Coal	Oil shale
Gasoline, % total liquid products.	87	90	89	87
Investment, $ per bbl. per day, gasoline.	6,500	8,200	8,500	8,400
Steel requirement ton per bbl. per day, gasoline	7.8	7.9	5.2	7.4

[1] Shale mined and retorted in Colorado. Raw shale oil transported by pipeline to California for refining.

Approximate cost of gasoline for maximum gasoline production

	Crude oil	Natural gas	Coal	Oil shale
Raw-material charge, assumed or estimated.	$2.78 per bbl.[1]	$0.10 per M cu. ft.[2]	$3.20 per ton.	$1.00 per ton.
Gasoline cost, cents per gal.:				
Raw material	8.8[1]	2.9[2]	3.9	4.2.
Manufacturing less credits	4.3	8.9	12.7	11.8.
Production, transportation.	1.0	1.0		
Total including 15% capital charges.	14.1	12.8	16.6	16.0.
Effect of increase in raw-material charge.	$1.00 per bbl. adds $0.032 per gal.	$0.10 per M cu. ft. adds $0.029 per gal.	$1.00 per ton adds $0.012 per gal.	$1.00 per ton adds $0.042 per gal.
Effect of 10% capital charge on investment in:				
Manufacturing	$0.016 per gal.	$0.037 per gal.		
Manufacturing and mining.			$0.056 per gal.	$0.055 per gal.

[1] Price delivered to refinery.

[2] Price in field after gathering.

Approximate investments and steel requirements for maximum middle-distillate production

Plant location	Gulf coast		Western Pa.	Colo.-Calif.
Product market area	Eastern seaboard			Calif.
Raw material	Crude oil	Natural gas	Coal	Oil shale
Investment $ per bbl. per day, total oil products	4,300	7,400	7,600	6,100
Steel requirements, ton per bbl. per day	5.7	7.1	4.6	5.7

2346. ———. Synthetic Fuels Picture. World Oil, vol. 128, February 1949, pp. 46–50. Petrol. Refiner, vol. 28, No. 3, 1949, pp. 95–96.

Some brief statistics are presented on the deposits and reserves of raw fuels in the United States, and approximate estimates of the investments required per unit of capacity for producing gasoline from crude oil, natural gas, coal (based on Fischer-Tropsch process), and oil shale are made. From a straight economic standpoint, it is believed that the production of liquid fuels from natural gas is competitive today with production of similar products from crude oil. With further improvements in manufacturing technique and possibly in mining or with further increases in the cost of finding and producing crude oil, production of liquid fuels from coal and oil shale may well become quite attractive from a cost standpoint. Substantial progress is bound to result from the large amount of research and development now being carried out.

2347. **Murphree, E. V., Gohr, E. J., and Kaulakis, A. F.** Applications of the Fluid Solids Technique to Producing Synthetic Liquid Fuels. Jour. Inst. Petrol., vol. 33, 1947, pp. 608–620. Petrol. Processing, vol. 3, 1948, pp. 355–361; Chem. Abs., vol. 42, 1948, p. 3162.

This paper, which was read before the 11th International Congress of Pure and Applied Chemistry, explains the basic elements of the fluid solids technique and describes 3 special applications of this development in the petroleum field, namely, the catalytic processing of gas oils, the extraction of liquid fuels from shale, and the synthesis of the higher hydrocarbon homologs from natural gas. Simplified diagrams showing the basic features of the above processes are shown. Other applications are under active development, among which are the coking of residual fuel oils and the carbonization and gasification of coal.

2348. Muszkat, K. [Synthesis of Liquid Hydrocarbons From Water Gas.] Przemysl Chem., vol. 18, 1934, pp. 483–489; Chem. Abs., vol. 29, 1935, p. 6022.

Most active catalyst, consisting of 4:1 Ni–SiO_2, loses 80% of its activity after 50 hr., while 9:1 Ni–BaO, Ni–ThO_2, and Ni–Al_2O_3 are virtually as active as at the beginning. Coating of the catalyst surfaces with the hydrocarbons produced does not affect its activity. All catalysts examined are instantly inactivated by O_2 in the reaction mixture.

2349. Myddleton, W. W. [Synthetic Internal-Combustion Motor Fuels.] Chim. et ind., vol. 37, 1937, pp. 863–864; Chem. Abs., vol. 31, 1937, p. 5975.

Brief discussion bringing out the superiority of the motor fuel, from the standpoint of its performance in the motor, produced by the British process (using water gas directly) over that produced by the Fischer process (using a gas mixture adjusted to a ratio of $2H_2:1\ CO$). The latter process could be improved by using Ni in place of Co, water gas in place of gases rich in H_2, and by operating in several steps.

2350. ———. Production of Hydrocarbon Oils From Industrial Gases. Colliery Guard., vol. 157, 1938, pp. 286–290; Jour. Inst. Fuel, vol. 11, 1938, pp. 477–492; Oel u. Kohle, vol. 14, 1938, pp. 723–726, 761–763; Chem. Age, vol. 38, 1938, pp. 404–407; Chem. Abs., vol. 32, 1938, p. 8105.

Process described is owned by Synthetic Oils Limited and is similar to the Fischer-Tropsch process. It is just entering upon a semiscale operation, a plant being under construction that will treat about 200,000 cu. ft. of gas per day, with an estimated yield of 180 gal. of oil. The process differs somewhat from the Fischer-Tropsch process. In the first place, by limiting the hydrogenation of the primary oil of synthesis, olefins rather than saturated hydrocarbons are produced, thus increasing the antiknock value of the motor fuel and producing more oils that can be converted into lubricants. This is partly accomplished by reducing the initial partial pressure of the H_2 in the reaction mixture, and partly by using a Co catalyst of less activity than that usually employed in the Fischer-Tropsch process. A gasoline has been produced with an octane no. of 68 and containing 70% olefins. It has also been found unnecessary to maintain in the synthesis gas the ratio $CO:H_2=1:2$; the conversion works satisfactorily at ratios between 1:1 and 1:1.5 making possible the direct use of blue water gas or Pintsch gas with a resultant reduction in cost. Furthermore, it is claimed that the catalyst used is stable to S, and that such slight poisoning as may occur has a beneficial effect in reducing the activity of the catalyst and promoting olefin formation. Even with 25 grains of S per 100 cu. ft., the catalyst has functioned satisfactorily.

2351. ———. Application of Free-Energy Equations to the Study of the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen. Jour. Inst. Petrol., vol. 30, 1944, pp. 211–224, 248.

Equations have been derived relating free energy of reaction to temperature in the synthesis of a series of gaseous hydrocarbons from CO and H_2. In building up these equations, molecular heat-temperature curves were drawn for each reactant and product and molecular heat-temperature equations were fitted over the range 25°–250° C., existing equations being generally unsatisfactory for the temperature range covering synthesis. Some use has been made of molecular heat and entropy values calculated from statistical and spectroscopic data. The suppression of reactions in which CO_2 is formed, in spite of free-energy changes favorable to them, is attributed to special conditions prevailing at the catalyst surface. The appearance of traces of ethylene among the products of synthesis instead of appreciable quantities predicted by the free-energy relationships is accounted for by the incorporation of ethylene actually formed into the building up of hydrocarbon chains. The possibility of increasing the yields of isobutane and isobutene is considered worthy of attention. The formation of aromatic hydrocarbons requires a special orientation of reactants on the surface of the catalyst, and the probability of the necessary conditions occurring is slight.

———. *See* abs. 9.

Myddleton, W. W., and Walker, J. Production of Hydrocarbon Oils From Industrial Gases. II. *See* abs. 10.

N

2352. Naeser, G. [Heat of Formation of the Iron Carbide Fe_3C.] Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf, vol. 16, No. 1, 1934, pp. 1–7; Chem. Abs., vol. 28, 1934, p. 2985.

Review of measurements of heat of formation of Fe_3C shows very variable values between positive and negative maximum. It was determined again from amorphous C and α–Fe at room temperature by converting the carbide (under separation of C) and the pure Fe into the iodide and chloride, respectively. From both methods, the heat of formation was found to be +8±0.25 kcal. per mol., which corresponds to 44.6±1.4 cal. per gm. cementite, 47.8±1.5 cal. per gm. Fe, 668±20 cal. per gm. C. The heat of combustion of finely distributed amorphous C on disintegration of carbide was found to be 107.9 kcal. per mol. The heat of reaction in the formation of FeS from α–Fe and rhombic S was 23.89±1.16 kcal. per mol. The final result is that the heat of formation of Fe_3C lies in the range of +8 to −4 kcal. per mol. according to the state of C and decreases with increasing graphitization. 46 refs.

2353. ———. [Specific Heat of the Iron Carbide Fe_3C.] Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf, vol. 16, 1934, pp. 207–210; Chem. Abs., vol. 29, 1935, p. 2434.

Heat contents of pure crystalline Fe_3C were measured between −190° and +770°, and average and true specific heats were calculated; the values are tabulated. The rule of additivity of atomic heats does not hold good for cementite. Heat of reaction of the magnetic transformation is about 1.5 cal. per gm. 18 rfs.

2354. ———. [Thermal Disintegration of Iron Carbide Fe_3C.] Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf, vol. 16, 1934, pp. 211–212; Chem. Abs., vol. 29, 1935, p. 2434.

Thermal disintegration of Fe_3C was determined by observing the behavior of cementite in a magnetic field as a function of temperature. Distintegration begins at 1,050°–1,060°.

———. *See* abs. 3675.

Nagai, H. *See* abs. 2504, 2508.

Nagasawa, K. *See* abs. 2211.

Nagel, R. H. *See* abs. 1469.

Nägeli, A. *See* abs. 1937.

Naicker, K. *See* abs. 3141.

Naiditch, I. M. *See* abs. 1275.

Nakagawa, M. *See* abs. 1900, 1901, 1902.

2355. Nakai, A. Studies on the Fischer-Tropsch Synthesis. I. Activation of Cobalt Catalyst by Hydrogenation. U. S. Naval Tech. Mission to Japan, X–38(N)–7, Encl. (B) 19, 1946, pp. 171–178; PB 58,701.

Experiments were made to determine the best conditions for activation of the standard Fischer-Tropsch Co catalyst ($Co:MgO:ThO_2$: kieselguhr=100:8:3:200). The apparatus, the procedure, and the catalyst preparation by precipitation are described, and the experimental results are tabulated. The results disclose that activation by H_2 gas is highly satisfactory for this catalyst under conditions of 375°–380°, at an optimum space velocity of 2,500–3,750 and a reduction time of 1½–2 hr. A special apparatus and a method are described for determining the optimum degree of reduction. It is shown from the above conditions that for the strongest catalytic activity the reduced Co catalyst contains not only about 50% of metallic Co but also lower oxides of Co. It is also found that when the above catalyst is used for the synthesis of oil at normal pressure and 175°–390°, a gas contraction of 85% and a yield of more than 160 cc. of oil (specific gravity about 0.75) for each m.³ of water gas ($H_2:CO=2:1$) are obtained.

2356. ———. Studies on the Fischer-Tropsch Synthesis. II. Studies on Iron Catalyst. U. S. Naval Tech. Mission to Japan, X–38 (N)–7, Encl. (B) 19, 1946, pp. 179–181; PB 58,701.

Experiments were made to investigate the effectiveness of iron catalysts for synthesis of oil from water gas at normal pressure. Reference is made to previous work of Tsuneoka on iron catalysts. The influence of metals or their oxides on the catalytic activity of the catalysts Fe:Cu:kieselguhr:Na_2CO_3=100:20:200:4 and Fe:Cu:ThO_2:kieselguhr:Na_2CO_3=100:20:4:200:4 was investigated, and various compounds were tested as promoters. MgO was found to be most effective. The most satisfactory catalyst at lower reaction temperatures of 235°–240° was Fe:Cu:ThO_2:MgO:kieselguhr:Na_2CO_3=100:20:4:20:175–200:4. To activate the catalyst, it was best to circulate water gas rapidly at the reaction temperature. The yield of synthetic oil with this iron catalyst was 61.6 gm. per m.³ of water gas ($H_2:CO=6:4$) at 235°, atmospheric pressure, and gas space velocity of 41 per hr.

2357. ———. Studies on the Fischer-Tropsch Synthesis. III. Studies on Liquid-Phase Synthesis With Iron Catalyst. U. S. Naval Tech. Mission to Japan X–38(*n*)–7, Encl. (B) 19, 1946, pp. 183–186; PB 58,701.

Investigation of a method for removing reaction heat from the synthesis apparatus by circulating the synthetic oil through the reaction system. Experiments were made to determine the activity of Fe catalysts in the liquid-phase synthesis. Various Fe catalysts were prepared by precipitation from nitrate mixtures with an excess of NaOH. Fe–Cu catalysts, containing small amounts of alkali, had a strong synthesis activity at temperatures under 250°. A similar catalyst, but containing no alkali, showed a weaker activity for oil synthesis but strong hydrogenating power at 250°–270°. The best catalyst for the liquid phase reaction appeared to be Fe:Cu:CaO=100:25:100–150. The catalysts Fe:CaO=100:100–150 and Fe:Cu:CaO=100:25:100–150 could be made into very hard tablets suitable for liquid-phase synthesis at 260°–270° and 10 kg. per cm.² pressure. The catalysts Fe:CaO=100:10 and Fe:Cu:CaO=100:25:10 had better activity than the above, but binders were required to make satisfactory tablets.

Nakbayashi, T. *See* abs. 1911, 1912.

2358. Namyslowski, S. [Problem of Synthetic Fatty Acids.] Przemysl Rolny i Spozywczy., vol. 4, 1950, pp. 173–177; Chem. Abs., vol. 45, 1951, p. 4062.

Review of the methods of oxidation of paraffins. It is estimated that 1,500,000 tons of the paraffin fraction from Fischer-Tropsch synthesis will be needed for covering the Polish demand for technical fats.

2359. Naphthali, M. [Methanol. Coal Liquefaction, Combined Hydrogenating and Cracking Processes.] Gas- u. Wasserfach, vol. 72, 1929, pp. 1178–1184; Chem. Abs., vol. 24, 1930, p. 942.

Review of patents and literature on the Bergius and I. G. Farbenindustrie processes of coal liquefaction, MeOH synthesis, and hydrogenation of hydrocarbons. The construction and heating of high-pressure reaction vessels are reviewed.

2360. ———. Fischer-Tropsch Process for Production of Synthetic Gasoline. Refiner and Nat. Gasoline Mfr., vol. 17, 1938, pp. 47–51; Chem. Abs., vol. 32, 1938, p. 4319.

Description of process, effect of varying operating conditions, and properties of products.

Narracott, E. S. *See* abs. 259.

2361. Nartowski, B. [Synthetic Fuels in Poland.] Nafta, vol. 2, 1946, pp. 344–345; Chem. Abs., vol. 43, 1949, p. 3591.

Discusses prospects for a synthetic motor-fuel industry in Poland based on the Fischer-Tropsch process.

2362. Nash, A. W. Recent Developments in the Formation of Synthetic Fuel From Carbon Monoxide and Hydrogen. Chem. and Ind., vol. 45, 1926, pp. 876–878; Chem. Abs., vol. 21, 1927, p. 638.

Review and brief discussion of theory and practical application of Fischer-Tropsch process.

2363. ———. Reports on the Progress of Naphthology During 1926. Synthetic Fuels. Jour. Inst. Petrol. Technol., vol. 13, 1927, pp. 597–601; Chem. Abs., vol. 21, 1927, p. 3734.

Brief review of developments.

2364. ———. Possible Auxiliary Sources of Liquid Fuels. Jour. Inst. Petrol. Technol., vol. 13, 1929, pp. 681–712; Chem. Trade Jour., vol. 81, 1927, pp. 205–207; Chem. Age., vol. 18, 1927, pp. 338–339; Chem. Abs., vol. 22, 1928, p. 152.

Discusses power alcohol, low-temperature carbonization of coal, the Bergius process, and the conversion of water gas into liquid fuels.

2365. ———. Synthetic Fuels and Lubricating Oils. Trans. World Power Conf., 1st Conf., Tokyo, 1929, pp. 466–481, 573–574; Chem. Abs., vol. 26, 1932, p. 2298.

Present known methods for production of synthetic fuels are described, and the oils are critically compared with their competitive petroleum products.

2366. ———. Reports on the Progress of Naphthology. Synthetic Fuels. Jour. Inst. Petrol. Technol., vol. 16, 1930, pp. 313–324; British Chem. Abs., 1930, B, p. 699.

Progress of research during the last 2 yr. concerning the Bergius process and the production of liquid hydrocarbons from gases.

2367. ———. Synthetic Fuels and Lubricating Oils. Jour. Inst. Fuel, vol. 3, 1930, pp. 347–353; British Chem. Abs., 1930, B, p. 849.

Paper was presented at the World Power Conference, Tokyo, in 1929. The sources and methods available for the production of synthetic fuels and lubricating oils are discussed. It is pointed out that the reduction of CO by H_2 at atmospheric and high pressures with or without catalyst is a possible source of fuel.

———. *See* abs. 817, 818, 843, 3258, 3259, 3260.

2368. Nash, A. W., and Bowen, A. R. Reports on the Progress of Naphthology During 1927. Synthetic Fuels. Jour. Inst. Petrol. Technol., vol. 14, 1928, pp. 643–650; Chem. Abs., vol. 23, 1929, p. 266.

Synthetic fuels from coal (berginization), CO and CH_4, or natural gas are reviewed briefly, indicating the hydrogenation of coal as most promising.

2369. Nash, A. W., and Stanley, H. M. Possible Chemical Utilization of Methane, With Special Reference to Natural Gas. Fuel, vol. 7, 1928, pp. 397–401; Chem. Abs., vol. 22, 1928, p. 4772.

In considering the various possibilities of its chemical utilization, a survey of the present knowledge of the properties of CH_4 is made. Its chlorination, oxidation, thermal decomposition, reaction with steam, and conversion into higher hydrocarbons are discussed. It is believed that the solution of this problem lies within the range of high-pressure and high-temperature reactions, which are now imperfectly understood.

2370. Natanson, G. L. [Genesis of Iron Catalysts for the Synthesis of Ammonia.] Jour. Chem. Ind. (U. S. S. R.), vol. 13, 1936, pp. 401–405; Chem. Abs., vol. 30, 1936, p. 4630.

Most important point in the preparation of NH_3 catalysts is the formation of a solid solution of the promoter in the catalyst, since in this case smaller crystals are formed and a more-porous product is obtained.

2371. Nathan, F. L. Fuel for Internal-Combustion Engines. Jour. Soc. Chem. Ind., vol. 46, 1927, pp. 211–220T; Chem. Abs., vol. 21, 1927, p. 2974.

Present and possible future sources, production, manufacture, utilization, and comparative costs of petroleum, gasoline, benzene, tetralin, EtOH, Natalite, liquid fuels from coals, MeOH, synthol, coal gas, and producer gas for use as motor fuels are reviewed and discussed from both national and world production and consumption standpoints. Apparently gasoline will continue for a long time to be the principal liquid fuel, especially in view of the enormous quantities of known oil shales existent. Only limited quantities of benzene and naphthalene, for tetralin, are ever likely to be available. Alcohol from whatever sources cannot compete as a fuel with gasoline at anything like present prices. Low-temperature carbonization and hydrogenation of coal and the production of synthetic fuels from CO and H_2 may soon become important means of liquid-fuel supply. Suction gas producers, using anthracite, coke, or charcoal, should be developed, especially for use with motor lorries.

2372. National Petroleum News. Diesel Fuel From Fischer Process. Vol. 31, 1939, No. 28, R, p. 296.

Synthetic fuel for high-speed diesel engines is now being produced in Germany on a commercial scale, according to a recent report to the U. S. Department of Commerce from the American Consulate General, Frankfort-am-Main. The process uses as raw material a mixture of tar oils produced in the coking of bituminous coal and so-called "Kogasin II," a material produced from gasified coke or CO and H_2. The Rheinpreussen Coal Mining Co. established the 1st large-scale plant for producing this fuel. The new fuel is handicapped by high cost. For giving market protection to the new synthetic product, the German Government again raised the import duty upon foreign diesel oil by 20% to a total of 12 from RM 9.6 per 100 kg., involving an increase in market price of 10–12%. Imports provide about 90% of Germany's requirements for diesel oil. These have increased considerably in recent years, being nearly 4 times as great in 1938 as in 1932. Imports in 1938 were close to 10,800,000 bbl.

2373. ———. Diesel Fuels From the Synthine Process. Tech. Sec., vol. 36, No. 36, Sept. 6, 1944, p. R585; Fuel Abs., May 1945, no. 2436.

Synthine (Fischer-Tropsch) process is a source of diesel fuels, which surpass any made from crude petroleum. Fischer-Tropsch oils are highly paraffinic, and those boiling at 200°–300° have a cetane number of 100, and, when diluted with tar oils or heavy petroleum oils, give a satisfactory Diesel fuel. A diesel-fuel fraction of about 85 cetane no. can be prepared by cracking Fischer-Tropsch wax. Straight Synthine diesel fuels have a drawback in their high solidification point, about 2° C. The cost of Synthine diesel fuels is higher than that for petroleum-derived diesel fuels, but extensive research has been conducted for some years by several companies, and lower costs should result. It is reported that the Texas Oil Co. is to construct a pilot plant for the Synthine process at its Los Angeles refinery. The process offers a new way of obtaining high-ignition-quality fuels without upsetting the balance of refinery-gasoline operation.

2374. ———. Plan to Build Synthetic-Oil Plant at Hugoton. Sept. 20, 1944.

Plans to build a Fischer-Tropsch plant to synthesize gasoline from natural gas in the Hugoton field, Oklahoma-Kansas, have been announced by Fred C. Koch, consulting engineer and partner in Winkler-Koch Engineering Co.

2375. ———. Petroleum Substitutes. Vol. 37, No. 36, 1945, p. R744; Business Week, July 21, 1945, p. 74.

Hydrocarbon Research, Inc., announces that it will construct a commercial Synthine (Fischer-Tropsch) plant in East Texas. The plant will have a capacity of 7,000 bbl. per day of finished products, 80–85% of which will be high-octane motor gasoline. Production will be at the rate of 1 bbl. of oil per 1,000 cu. ft. of gas. The process, developed in the past 20 mo., has been sponsored by 3 oil producers—the Magnolia Petroleum Co., the LaGloria Corp., and the J. S. Abercrombie Co. The process is based on German laboratory research applied to American oil-industry techniques concerning plant design and construction and the use of cheaper catalysts. The plant, it is said, will be constructed at a fraction of the cost of similar German plants and will produce a higher quality gasoline.

2376. ———. Bureau of Mines Takes Too Much Credit for Development of Synthetic Fuels. Vol. 38, No. 26, 1946, pp. 10–11.

Editorial polemic.

2377. ———. Domestic Use of Oxo Process Revealed. Vol. 38, 1946, p. R567.

Brief description of the Oxo process, and a statement of its possible adaptation by Standard Oil of Indiana for making higher-boiling alcohols from the olefins obtained by cracking petroleum-derived paraffin wax.

2378. ———. Fischer-Tropsch Process Patents Available for Licensing. Vol. 38, No. 8, 1946, p. 44.

Office of Alien Property Custodian has made available for licensing a group of patents relating to synthetic gasoline production by the Fischer-Tropsch process. The licenses are available on a royalty-free, nonexclusive basis for a $15.00 administrative fee. Full information and list of patents may be obtained from Patent Use and Development Section, Office of Alien Property Custodian, Washington 25, D. C.

2379. ———. Synthetic-Gas-Plant Construction Loan Authorized. Vol. 38, No. 19, 1946, p. 51.

Reconstruction Finance Corporation has authorized a loan of $9,000,000 to Carthage Hydrocol, Inc., to complete a plant at Brownsville, Tex., for synthesizing gasoline from natural gas. Total cost of the plant is about $20,000,000. Construction of the plant will be directed by Hydrocarbon Research, Inc., which controls patents under the Hydrocol process. The process is a modification of the Fischer-Tropsch process and has been improved through the development of low-cost O_2 to produce a low-cost, high-octane gasoline that will be competitive with that produced from petroleum. Operating under royalty-free patents, it is estimated that a 78–80 octane gasoline will be produced at slightly more than $0.04 per gal.

2380. ———. Synthetic Gasoline Plant Plans Studied by Stanolind Oil Co. Vol. 38, No. 28, 1946, p. 48.

Tentative plans are being studied by Stanolind Oil & Gas Co. to erect a synthetic gasoline plant, based on the Fischer-Tropsch synthesis of liquid hydrocarbons from CH_4 on the Kansas side of the Hugoton field. Plant will be designed to produce aproximately 6,000 bbl. gasoline per day and 1,200–1,500 bbl. diesel fuel from about 60,000,000 cu. ft. of natural gas. Actual construction date is uncertain. Stanolind has been conducting research and pilot-plant investigation for several years at its Tulsa laboratory. The process is not yet fully developed, and engineering designs are incomplete.

2381. ———. Synthine Developments Continue at Rapid Pace. Vol. 38, 1946, pp. R567–568.

Review of recent developments as reported in the current news.

2382. ———. Stanolind to Build 2 Plants to Make Chemicals From Gas. Vol. 39, No. 34, 1947, p. 16; Chem. Eng. News, vol. 25, 1947, p. 2436.

Stanolind Oil & Gas Co. will build chemical recovery and separation plants adjacent to each of the synthetic gasoline plants now under construction—Carthage Hydrocol near Brownsville, Tex., and the Stanolind plant, Hugoton, Kans.—to refine byproduct chemicals from them. A contract has already been made with United States Industrial Chemicals, Inc., for the sale of water-soluble oxygenated hydrocarbon chemicals to be produced. Furthermore, the latter will build its own plants at the 2 locations to manufacture an additional line of chemicals. Each of the synthetic gasoline plants will produce around 100,000,000 lb. per yr. of water-soluble oxygenated hydrocarbons. These chemicals consist mainly of straight-chain alcohols, aldehydes, acids, and ketones containing 2–4 C atoms per mol. Stanolind has not yet completed its plans for refining and marketing the higher molecular weight alcohols, acids, aldehydes, and ketones containing 5–12 or more C atoms. The chemical recovery and separation plants are expected to be completed in about 2 yr. The cost of the plant is not given. It is estimated that the chemicals from the 2 synthetic gasoline plants may exceed a total of 300,000,000 lb. per yr. Commodities to be produced are listed.

2383. ———. Synthetics Subsidy? Vol. 39, No. 31, 1947, p. 5.

Editorial.—The possibility is being discussed in government research circles that, once technology of synthetic liquid-fuels research is developed to the point where commercial production can be planned, the Federal Government may consider granting subsidies for construction and operation of privately-owned plants. This would be following the pattern of other countries—England, Sweden, France, Australia—which made Government grants to private plants for production of liquid fuels from coal and oil shale. Subsidies, it is said, will be needed because oil from coal and shale probably will not be competitive with conventional liquid fuels for some time. However, there is a possibility that the Government itself may build several commercial-type plants—each with production capacity of 5,000–10,000 bbl. per day—to test various coal hydrogenation, Fischer-Tropsch, and oil-shale processes.

2384. ———. Texaco Offers to License Hydrocol Process. Vol. 40, No. 6, 1948, p. 49.

Texas Co., through its affiliate Texas Development Corp., will license the Hydrocol process for manufacture of synthetic liquid hydrocarbons to any interested company. The opinion is expressed that 50 plants for gasoline synthesis from natural gas, with combined output of 350,000 bbl. per day might be built within 10 yr., barring non-economic acceleration of program to meet national defense requirements. The limiting factor is the number of gas pools large enough to support an economical plant. Without infringing on gas supplies earmarked for other uses, 50 plants of 7,000 bbl. per day capacity can be built. Liquid fuel from natural gas probably will meet about 5% of the total demand for all oils by 1960. A 5,000-gal. per day Hydrocol pilot plant has been completed at Montebello, Calif., and work is being done on gasification of coal and heavy oil, but not on oil from shale. The company spent approximately $1,000,000 in 1947 on synthetics research and will do the same in 1948.

2385. Natta, G. [Relation of the Activity of Proposed Catalysts for the Synthesis of Methyl Alcohol and Their Chemical and Crystalline Structure.] Giorn. chim. ind. applicata, vol. 12, 1930, pp. 13–23; British Chem. Abs., 1930, A, p. 552; Chem. Abs., vol. 24, 1930, p. 2717.

Catalysts available are: (1) Cu salts, which are easily poisoned by S compounds; and (2) Zn salts, which, alone, soon lose their activity. However, certain oxides, notably Al_2O_3, and especially Cr_2O_3, by acting as protecting colloids, prevent the crystallization of the ZnO with its consequent loss of activity. Above 500°, these oxides begin to form spinels, and therefore lose some of their protective action. Some oxides form solid solutions with ZnO by entering its space lattice. The oxides of bivalent metals whose ionic diameter is 0.6–0.9 Å. U. Mg, Ni^{II}, Cu^{II}, Co^{II}, Fe^{II}, and Mn^{II} are included. Cu and Ni are reduced to metal, the former helping, the latter hindering the catalysis. Of the oxides entering the space lattice, those causing most deformation, that is, whose diameters are further from that of ZnO, are most effective; FeO is most effective. The alkali and alkaline earth oxides, because of their basicity, promote not only the formation of MeOH, but of other organic products as well, especially higher alcohols.

2386. Natta, G., and Casazza, E. [Activity of Catalysts Proposed for the Synthesis of Methanol and Their Chemical and Crystalline Structure. II.] Giorn. chim. ind. applicata., vol. 13, 1931, pp. 205–212; Chem. Abs., vol. 26, 1932, p. 80.

Coefficients of absorption of CO_2, CO, and H_2 by substances, which have been used as catalysts in the production of MeOH have been studied. Pure ZnO (1), ZnO derived from smithsonites from various sources (2), reduced $ZnCrO_4$ (3), Cr_2O_2 (4), 50 ZnO–1Co (5), 5ZnO–1Cu (6), 4 ZnO–$1Al_2O_3$ (7), and 5ZnO·1MgO (8) were all studied. Those catalysts that absorb high amounts of H_2 (4, 5, 6) are not efficient as they catalyze side reactions involving hydrogenation, while those showing high CO_2 and CO absorption with low H_2 absorption, that is, (2, 7), are most effective. The absorption increases with increasing pressure up to 35–40 atm. Above this the absorption curve becomes virtually horizontal, increasing pressure having practically no effect.

2387. Natta, G. [Synthesis of Methanol and Higher Alcohols From Water Gas.] Österr. Chem.-Ztg., vol. 1937, pp. 162–170; British Chem. Abs., 1937, B, p. 756; Chem. Abs., vol. 31, 1937, p. 5978.

Curves showing the equilibrium constant and velocity constant for the synthesis and the decomposition of MeOH are given. The synthesis is a trimolecular reaction. The best catalyst is ZnO obtained by heating natural smithsonite at 350°. The calcined catalyst has a porosity of 47%, high mechanical strength, and will absorb 10,000 vol. of CO_2 at low pressures. With calcined smithsonite impregnated with K acetate as a catalyst and a gas containing an excess of H_2, CH_3OH, and higher alcohols are obtained. If the gas contains an excess of CO, the alcohols contain a high % of ketones, aldehydes, and acids. Reactions are given and experimentally verified in which the alkali in the contact mass acts directly in the formation of the higher alcohols. The higher alcohols contain high % of isobutanol and *n*-PrOH and low % of EtOH iso-PrOH and *n*-BuOH. MeOH with ⅓ of its volume of higher alcohols is miscible in all proportions with benzine. MeOH requires 6.33 kg. air per kg., while benzine required 14.8 kg. air per kg. 10% of MeOH instead of 26% EtOH or 60% benzene is required to raise the octane value of a benzine from 66 to 80.

2388. ———. [New Large-Scale Organic Syntheses.] Chimica e industria, vol. 20, 1938, pp. 186–198; British Chem. Abs., 1938, B. p. 762.

Lecture in which industrial processes involving the syntheses of organic substances from C and from H_2 and O_2 (either in the elementary state or combined as H_2O) are summarized, for example, synthesis of water gas, MeOH, hydrocarbons, higher alcohols, CH_2O, explosives, and rubber.

2389. ———. [Preparation of Mono- and Polyhydroxy Alcohols.] Chimica e industria, vol. 24, 1942, pp. 389–393; Chem. Zentralb., 1943, I, p. 2242; Chem. Abs., vol. 38, 1944, p. 4252.

Some new methods of large-scale technical synthesis of mono- and poly-OH alcohols from water gas (MeOH synthesis) and from CO_2 and H_2 are described. In the latter case, the CO_2 is a byproduct in the production of $Ca(NO_3)_2$ from $CaCO_3$: the H_2 is produced by electrolysis. The yield of MeOH synthesized by this process reaches 92%, as compared with 86–89% by the usual water-gas process.

2390. Natta, G., and Boccaredda, M. [Motor Fuel of High Octane Number. Synthesis of Isooctane From Water Gas.] Riv. ital. petrolio, vol. 6, No. 65, 1938, pp. 14–19; World Petrol., vol. 10, 1939, p. 69; British Chem. Abs., 1939, B, p. 571.

Isobutylene, obtained by dehydrogenation of BuOH produced in the synthesis of MeOH from water gas, mixed with a small amount of gaseous HCl, is heated to 100°–250° and passed over solid Al_2O_3 previously activated by heating to 400°–450°. The isooctene produced is then hydrogenated to isooctane.

2391. Natta, G., and Pastonesi, G. [Kinetics of the Synthesis of Methanol.] Chimica e industria, vol. 19, 1937, pp. 313–318; Chem. Zentralb., 1937, II, p. 3297; Chem. Abs., vol. 31, 1937, p. 8337.

Equilibrium data for the synthesis of MeOH are best expressed assuming that the change occurs in 2 stages $CO+H_2=CH_2O$ and $CH_2O+H_2=MeOH$. The first equation is slow, while the second is almost instantaneous, so that analysis shows only a minimum of CH_2O present at any time. The equation of the reaction curve is expressed as

$$d(K'_2t)/dx=1/\{2(a-x)^2-[Kx/2(a-x)]\},$$

where a=partial pressure of CO, x=amount of CO converted in time t, and thus equals the amount of CH_2O formed. The heat of reaction is calculated as 21,000 cal.

2392. ———. [Kinetic Method for Determining the Equilibrium Constants in the Methanol Synthesis.] Chimica e industria, vol. 20, 1938, p. 587–591; Chem. Abs., vol. 33, 1939, p. 2023.

With the equation of Newton and Dodge (abs. 2457) for calculating the equilibrium constant of a reaction as a basis, a method was devised for calculating the constant for the synthesis of MeOH using experimental data for the partial pressures involved. Calculation is made assuming the synthesis to be a trimolecular reaction $MeOH=CO+2H_2$; and also assuming bimolecular reactions in 2 stages with the intermediate formation of CH_2O. The latter assumption gives data that approximate experimental determination of the equilibrium constant more closely.

2393. Natta, G., and Pino, P. [Some New Applications of the Oxo Synthesis.] Chimica e industria, vol. 31, 1949, pp. 109–111; British Abs., 1949, B, II, p. 943.

Oxo synthesis is a method of wide applicability for producing aldehydes from CO, H_2, and compounds containing an olefinic double bond in presence of metallic Co or CoI_2. Cyclic mono-olefins can be used as starting materials, and terpenes interact even more readily than do olefins. Esters may also be obtained. With metallic Co as catalyst, a long induction period occurs varying with the method of preparation and surface changes.

2394. Natta, G., and Piontelli, R. [Utilization of Methane in the Production of Hydrogen.] Chimica e industria, vol. 19, 1937, pp. 177–182; British Chem. Abs., 1937, B, p. 777; Chem. Abs., vol. 31, 1937, p. 8128.

Incomplete combustion of CH_4 in the presence of CO_2 and H_2O has been investigated in the temperature range 800°–1,400°. Complete equilibrium diagrams of the 2 systems $CH_4–H_2O–O_2$ and $CH_4–CO_2–O_2$, and the best conditions for producing H_2 and CO in the ratio of 2:1, are determined.

2395. Natta, G., and Rigamonti, R. [Synthesis of Aliphatic Alcohols by the Catalytic Reduction of Carbon Monoxide.] Giorn. chim. ind. applicata, vol. 14, 1932, pp. 217–225; Chem. Zentralb., 1932, II, p. 2264; Chem. Abs., vol. 26, 1932, p. 5062.

CO obtained from water gas was reduced with H_2 at 350–400 atm. in the presence of calcined ZnO, smithsonite, and KOAc as catalyst. The crude product contained only 0.9–1.1% aldehydes, 0.02–0.5% hydrocarbons, 1.4–2.4% free acids, and 2.5–2.6% ethers. Increasing the amount of K_2O in the catalyst increased the proportion of higher alcohols. The following alcohols were identified: Iso-Bu, 51.3–46.6; Pr, 13.1–11.6; β-methylbutyl, 4.9–4.8; Et, 3.3–4.2; iso-Pr, 2.6–3.7; β-methylpentanol, 2.5; Bu, 1.8–2.0; Am, 0.4; β-methylhexanol, 1.6%. Traces of the following also were identified: γ-methylpentanol, isoamyl alcohol, 2,3-dimethylbutanol, ethylisopropylcarbinol, diisopropylcarbinol, propylisopropylcarbinol, and tertiary Bu and Am alcohols. Of the total alcohols, 94.7–98.4% are primary, and those with an odd number of C atoms predominate in the straight-chain group, while the β–Me predominate in the side-chain group.

2396. ———. [Manufacture of Hydrogen by Conversion of Carbon Monoxide Under Pressure.] Chimica e industria, vol. 18, 1936, pp. 623–630; Chem. Abs., vol. 31, 1937, p. 2365.

Catalytic action of MgO and ZnO on the reaction $CO+H_2O \rightarrow CO_2+H_2$ has been determined. ZnO is much more effective than Mg as a catalyst. Addition of K_2CO_3 increases the % conversion at 363° from a value of 58.8% with ZnO to 93% with K_2CO_3, while 5% Na_2CO_3 raises the % conversion only to 78%.

2397. ———. [Gasification of Italian Fuels by Means of Oxygen.] Atti X° cong. intern. chim., vol. 4, 1939, pp. 312–319; Chem. Abs., vol. 34, 1940, p 2568.

Results of continuous retorting on a semi-industrial scale of coal, lignite, etc., containing volatile matter by means of mixtures of O_2 and steam, according to a process first applied to coal in volatile substances, are summarized. The process in 1 case led to the production of a very pure water gas most suitable for chemical syntheses (MeOH, higher alcohols, Fischer gasoline, etc.), for conversion and for the production of H_2, and synthetic NH_3.

2398. Natta, G., and Strada, M. [Synthesis of Alcohols Higher Than Methanol From Water Gas.] Giorn. chim. ind. applicata, vol. 12, 1930, pp. 169–174; Chem. Zentralb., 1930, II, p. 659; Chem. Abs, vol. 24, 1930, p 4505.

In the presence of ZnO, active form made by calcining certain smithsonites at low temperature, together with alkali (K, Rb, Ce) carbonate, hydroxide, acetate or propionate, water gas, when heated to about 400° under high pressures, gives a mixture of higher alcohols free of CH_4 and other hydrocarbons. Metals of groups 4–8, as well as their oxides, should be excluded so as to avoid formation of undesirable byproducts, particularly hydrocarbons. The formation of higher alcohols occurs in stages, MeOH being first formed, then MeOK, or Rb, Ce, then addition of CO_2 to form the higher homolog. These intermediate products were identified during the course of the reaction, and these can be added as additional catalysts, which retain their activity over long periods of time.

2399. ———. [Synthesis of Aliphatic Alcohols From Mixtures of Carbon Monoxide and Hydrogen.] Giorn. chim. ind. applicata, vol. 13. 1931, pp. 317–325; Chem. Zentralb., 1931, II. p. 1958; Chem. Abs., vol. 26, 1932, p. 693.

Experiments carried out on a semi-industrial scale show that in the presence of catalysts consisting of compounds of Zn and the alkali metals CO and H_2 will react under pressure to form aliphatic alcohols. By excluding any metals of groups 4–8, many harmful secondary reactions, as formation of CH_4 are reduced greatly. The hypothesis that MeOH is first formed and reacts with CO to form higher homologs is strengthened by the observation that in the presence of HCO_2K a higher yield of MeOH is obtained, while CH_3CO_2K and $EtCO_2K$ increase the yields of EtOH and PrOH, respectively.

2400. ———. [Low-Temperature Production of Coal Gas by Using Oxygen.] Giorn. chim. ind. applicata, vol. 14, 1932, pp. 76–86; British Chem. Abs., 1932, B. p. 407; Chem. Abs., vol. 26, 1932, p. 3359.

Coals with low volatile contents may be heated at 700°–800° by using O_2; the gases produced are rich in H_2 and CO and very low in hydrocarbons and inert gases. Gases suitable for the synthesis of MeOH, that is, having a ratio H_2:CO of 1.5:4, may be obtained by burning 0.28 kg. C in 0.18 m.³ of O_2 at about 750°.

2401. Natta, G., Pino, P., and Beati, E. [Considerations on the Oxo Synthesis.] Chimica e industria, vol. 31, 1949, pp. 111–113; British Abs., 1949, B. II, p. 998.

Probable mechanism of the reaction is discussed, based on kinetic measurements and thermodynamic considerations. The equilibrium constant is calculated for the synthesis of propionaldehyde from C_2H_4. Comparison is made with the Fischer-Tropsch reaction.

2401a. Natta, G., Pino, P., and Ercoli, R. Hydrogen Transfer Reactions Accompanying the Cobalt-Catalyzed Addition of Carbon Monoxide to Olefinic Compounds. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 4,496–4,498.

Co-catalyzed reaction of CO and olefins with alcohols and with amines normally yields esters and amides. In some instances, however, products containing added H_2 are formed. The H_2 is furnished by the reactants, possibly by way of the formation and decomposition of Co hydrocarbonyl.

2401b. Natta, G., Pino, P., and Mantica, E. [Synthesis of Esters by Reaction of Olefins, Carbon Monoxide, and Alcohols.] Gazz. chim. ital., vol. 80, 1950, pp. 680–701; Chem. Abs., vol. 46, 1952, p. 904.

Possible mechanisms of the carboxylation of olefins in the presence of CO are discussed. It is suggested provisionally that the catalytically active compound is Co hydrocarbonyl. It adds to the unsaturated bonds of the olefins with formation of intermediate compounds, which, in their turn, react with compounds containing mobile H atoms.

2402. Natta, J. [Synthesis From Carbon Monoxide. I., II. Synthesis of Methanol, of Higher Alcohols and of Fuel, and the Oxo Process.] Industria y quim., vol. 11, 1949, p. 115; vol. 12, 1950, pp. 2–3; Chem. Zentralb., 1951, I, p. 3287.

MeOH synthesis as practiced in the plant at Rio Tercero, Argentina, is described. Fischer-Tropsch synthesis in the United States with fluidized catalysts also is reported.

2403. Naudain, E. [Synthetic Liquid-Fuel Industry.] Ind. chim., vol. 23, 1936, pp. 82–85, 162–169, 247–249; Chem. Abs., vol. 30, 1936, p. 4647.

Review.

2404. ———. [Industries Based on Syntheses From Coke-Oven Gas.] Tech. ind. chim., No. 277, 1938, pp. 20–26; Chem. Abs., vol. 33, 1939, p. 3113.

Syntheses of NH_3 MeOH, gasoline, and C_2H_4 derivatives are discussed.

2405. Naumann, F. K. [Steels for Plants Producing Motor Fuels.] Chem. Fabrik, vol. 11, 1938, pp. 365–376; Chem. Abs., vol. 32, 1938, p. 7387.

Fischer benzine synthesis at low pressures and temperatures requires no special steel equipment, but cracking processes up to 70 atm. and 600° require steels with special resistance to attack by H_2S and to high temperatures. Hydrogenation up to 700 atm. places still higher requirements on steels, the extent to which alloyed steels meet these demands was investigated, and some effects on chemical composition and physical properties are shown by 18 graphs, 22 photomicrographs and numerous cuts. A plan of equipment for test steels in H_2 up to 1,000 atm. is given. 12 refs.

2406. ———. [Steels Used in Plant for Production of Motor Fuel.] Tech. Mitt. Krupp, vol. 6, 1938, pp. 77–87; British Chem. Abs., 1938, B, p. 1307.

Compositions and properties of steels used in apparatus for the cracking of petroleum, the high-pressure hydrogenation of coal, and the production of hydrocarbons by the Fischer-Tropsch process are reviewed.

Naumova, A. I. *See* abs. 893.

2407. Nauss, O. [Enhancing the Value of Coal.] Gas- u. Wasserfach, vol. 70, 1927, pp. 832–834.; Chem. Abs., vol. 21, 1927, p. 3728.

Review of the use of coal as a raw material for the production of low-temperature coke, tar, oils, and gas of high calorific value, as well as the hydrogenation of coal (Bergius process) and the Fischer synthesis of hydrocarbons.

2408. Navarre, R. [Lubricant Substitutes.] Chim. et ind., vol. 48, 1942, pp. 295–301, 355–360; Chem. Zentralb., 1943, I, p. 2165; Chem. Abs., vol. 38, 1944, p. 4417.

After a detailed survey of the lubricant needs of France, it is agreed that of the various possibilities for their procurement, the order is: The petroleum industry, oil from coal, shale oil and rosin, and polymerization of olefins or unsaturated hydrocarbons obtained from Fischer-Tropsch synthesis.

2409. Nay, M. A., and Morrison, J. L. Molecular Adsorption Areas of Hydrocarbon Gases on Charcoal. Canadian Jour. Research, vol. 27, B, No. 4, 1949, pp. 205–214.

Low-temperature adsorptions of CH_4, C_2H_6, C_3H_8, $n–C_4H_{10}$, iso–C_4H_{10}, C_2H_2, C_2H_4, and N_2 on a series of coconut charcoals of different degrees of activation were determined. Langmuir isotherms were obtained in every case. The measurements indicate horizontal orientation of the hydrocarbon molecules on the charcoal surface. By comparing the maximum number of millimoles adsorbed for each gas on each charcoal with the respective maximum number of millimoles of N_2 adsorbed, and by assuming a molecular adsorption area of 16.2 square Ångstroms for N_2, the following average molecular adsorption areas were obtained: CH_4, 19.4; C_2H_6, 25.9; C_3H_8, 36.0; $n–C_4H_{10}$, 42.1; iso–C_4H_{10}, 47.4; C_2H_2, 19.8; and C_2H_4, 23.1 square Å.

2410. Nedelmann, H. Hydrogenation and Fischer-Tropsch Synthesis. Chem. Ind., vol. 1, No. 2, 1949, pp. 62–64.

Status of synthetic fuel production in Germany and the effect of dismantling the plants on the German economy are discussed.

2411. Negishi, R. Qualitative Consideration on the Mechanism of Synthesis of Higher Alcohols From Carbon Monoxide and Hydrogen and From Lower Alcohols. I. Mechanism for Primary Alcohols. Rev. Phys. Chem. Japan, vol. 18, 1944, pp. 47–57; Chem. Abs., vol. 41, 1947, p. 4770.

From the already established results that BuOH is obtained from 2 mol. EtOH, PrOH from EtOH and MeOH, and $MePrCH_2OH$ from EtOH and iso–PrOH, the mechanism of synthesis of higher alcohols from lower alcohols in the presence of CaC_2 can best be explained by Graves' extension of Guerbet's direct dehydration theory except for the modification that a H atom of $—CH_3$ reacts readily, provided the $—CH_3$ is in the α position (adjacent to the carbinol radical).

2412. ———. Qualitative Consideration on the Mechanism of Synthesis of Higher Alcohols From Carbon Monoxide and Hydrogen and From Lower Alcohols. II. Mechanism for Secondary Alcohols and the Comparison of Different Mechanisms. Rev. Phys. Chem. Japan, vol. 18, 1944, pp. 58–70; Chem. Abs., vol. 41, 1947, p. 4770.

After discussing Fischer-Tropsch's intermediate acid theory, Morgan and coworkers' aldol condensation theory, and Frolich's and Graves' modifications of Guerbet's direct dehydration theory, the author supports the last as the most probable mechanism of synthesis of higher alcohols from lower alcohols or from CO and H_2, with the concession that the aldol condensation may take place if aldehydes and ketones are formed during the synthesis as secondary reactions.

———. *See* abs. 2420.

Negishi, R., and Kamiike, O. Hydrocarbons From Carbide. IV. Noncatalytic Polymerization Under Ordinary Pressure. Acetylene-Carbide System and General Remarks. *See* abs. 2417.

———. Hydrocarbons From Carbide. V. Noncatalytic Polymerization Under Ordinary Pressure—Acetylene Carbide Systems. *See* abs. 2423.

———. Hydrocarbons From Carbide. III. Noncatalytic Polymerization Under Ordinary Pressure—Carbon Dioxide-Carbide Systems. *See* abs. 2421.

———. Hydrocarbons From Carbide. V. Noncatalytic Polymerization Under Elevated Pressure. Comparison Between Ordinary and Elevated Pressure Reactions. *See* abs. 2418.

———. Hydrocarbons From Carbide. VI. Noncatalytic Polymerization Under Ordinary Pressure—Considerations and Comparisons Between Nascent and Ordinary Acetylene Polymerizations. *See* abs. 2424.

———. Hydrocarbons From Carbide. II. Noncatalytic Polymerization Under Ordinary Pressure. Hydrogen Systems and General Experimental Details. *See* abs. 2415.

———. Hydrocarbons From Carbide. III. Noncatalytic Polymerization Under Ordinary Pressure. Systems of Calcium Carbide With Carbon Dioxide, Carbon Monoxide, and Hydrogen Chloride. *See* abs. 2416.

2413. Negishi, R., and Sakon, K. Heat of Reaction in the Synthesis of Hydrocarbons From Carbide. Jour. Chem. Soc. Japan, vol. 64, 1943, pp. 1515–1522; Chem. Abs., vol. 41, 1947, p. 3359.

Utilization of the heat of reaction of carbide with H_2, CO_2, and H_2O for the cracking of fluid paraffin was studied. In the synthesis of isobutanol from the mixture of CO and H_2 at 320° in the presence of carbide, the heat of reaction is found to be 179 kcal. per mol. of carbide. Absorption of the heat of reaction takes place by cracking of fluid paraffin; the temperature of the reaction mixture remains uniform.

Negishi, R., Kamiike, O., and Kataoka, S. Hydrocarbons From Carbide. IV. Noncatalytic Polymerization Under Ordinary Pressure—Carbon Monoxide–Carbide System and Hydrogen Chloride–Carbide Systems. *See* abs. 2422.

2414. Negishi, R., Kimura, O., and Kamiike, O. Hydrocarbons From Carbide. Rev. Phys. Chem. Japan, vol. 15, 1941, pp. 31–41; Chem. Abs., vol. 35, 1941, p. 6501.

Many hydrocarbons can be synthesized directly from CaC_2, without first preparing C_2H_2 to be polymerized later. The free energy of formation is calculated for a number of chain hydrocarbons and cyclic hydrocarbons, both from CaC_2 and H_2O to produce hydrocarbon and CaO and also from CaC_2, CO, and H_2 to form hydrocarbon and $CaCO_3$. The free-energy changes are very large, especially for the hydrocarbons with the greater number of C atoms. The ΔF at 300° is 83.5 kg.-cal. greater for the preparation of benzene from CaC_2 and H_2O, than from C_2H_2, and the increase in ΔF is even larger for similar syntheses of 1,3–butadiene or *n*–octane. The affinity of CaC_2 for H_2O, and of CaO formed during the reaction for CO_2, may increase the reaction rate by effectively removing these reaction products. The temperature coefficients of the reactions in which $CaCO_3$ is formed are greater than those in which CaO is formed. The addition of CaC_2 and the greater reactivity of nascent C_2H_2 molecules result experimentally in a faster rate and greater yield of polymerized C_2H_2 than is obtained by catalytic polymerization with a $Co–Ni–Cr_2O_3$ clay catalyst or a Fe–Ni–kieselguhr catalyst.

2415. Negishi, R., and Kamiike, O. Hydrocarbons From Carbide. II. Noncatalytic Polymerization Under Ordinary Pressure. Hydrogen Systems and General Experimental Details. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 118–125; Chem. Abs., vol. 41, 1947, p. 4434.

Study of the synthesis of hydrocarbons directly from carbide at 250°–450° has been carried out. Reaction at 340° proved to be most suitable for the synthesis of liquid hydrocarbons. The effects of temperature on the formations of the products are discussed. These effects are intimately associated with the heat of reaction involving the carbide.

2416. ———. Hydrocarbons From Carbide. III. Noncatalytic polymerization Under Ordinary Pressure. Systems of Calcium Carbide With Carbon Dioxide, Carbon Monoxide, and Hydrogen Chloride. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 244–251; Chem. Abs., vol. 41, 1947, pp. 4434–4435.

Effects of CO, CO_2, and HCl on the synthesis of hydrocarbon liquids directly from Ca carbide in the temperature range of 340°–420° have been studied. The results are in agreement in general with those in the H_2 system. The main reaction of the nascent C_2H_2 molecules is only slightly affected by the carrier gases. In the CO_2 system, the yield of liquid products has been found as high as 43% of the total reacted C_2H_2. CO_2 takes part only in the formation of CaC_2. The presence of H_2 seems to have no effect on the character of the liquid products. Whereas CO_2 has favorable effects, CO has unfavorable effects, and HCl has no effect at all on the yield of liquid hydrocarbons.

2417. ———. Hydrocarbons From Carbide. IV. Noncatalytic Polymerization Under Ordinary Pressure. Acetylene Carbide System and General Remarks.

Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 345–354; Chem. Abs., vol. 41, 1947, p. 4435.

Results of the series of investigations, on the systems H_2, CO_2, CO, HCl, and C_2H_2 with CaC_2 are given: CO has a harmful effect, although CO_2 has a beneficial effect; HCl gives somewhat harmful effects only when its concentration is high; and C_2H_2 increases the total yield because it polymerizes. When C_2H_2 is diluted with an inert gas, such as H_2 or CO_2, its effect on the total liquid yield disappears; the presence of a small amount of C_2H_2 has a striking effect on the suppression of the formation of free C_2H_2. [The nascent C_2H_2 molecules, which related to polymerization, are suggested to have the structure $n(C_2H_2)=(C_2H_2)_n$.] There are indications that the efficacy of the synthesis of hydrocarbon liquids from CaC_2 is higher than even the catalytic polymerization.

2418. ———. Hydrocarbons From Carbide. V. Noncatalytic Polymerization Under Elevated Pressure. Comparison Between Ordinary and Elevated Pressure Reactions. Bull. Chem. Soc. Japan, vol. 17, 1942, pp. 355–364; Chem. Abs., vol. 41, 1947, p. 4435.

Effects of species of gases, pressure, and temperature on the character and yield of liquid products in the synthesis of hydrocarbons from Ca carbide under high pressures have been studied. The yield of liquid products increases with increase of total pressure of the system up to about 100 atm. and then decreases with further increase in the pressure. In the low-pressure runs, CO has noticeably harmful effects, whereas CO_2 has beneficial effects on the yield of liquid products. There are slight differences in the yields and the properties of the products under elevated and ordinary pressures, and these differences are explained as owing rather to the effects of the time of contact and temperature than to any change in the mechanism of the polymerization reaction.

Negishi, R., Nibayashi M., and Kamiike, O. Hydrocarbons From Carbide; Noncatalytic Polymerization Under Elevated Pressure. II. Hydrogen–Carbide and Water Gas–Carbide System. *See* abs. 2426.

2419. Negishi, R., Kataoka, S., Kamiike, O., and Nibayashi, M. Hydrocarbons From Carbide. I. Noncatalytic Polymerization Under Ordinary Pressure—Hydrogen–Carbide Systems. Jour. Soc. Chem. Ind. (Japan), vol. 44, suppl. binding, 1941, pp. 450–451 (in English); Chem. Abs., vol. 44, 1950, p. 8853.

Liquid hydrocarbons have been obtained directly from carbide with H_2 as a carrier gas for water vapor. Satisfactory yields were obtained at 340°–420° and a saturation temperature of 80°. There is an optimum grain size of the carbide; smaller grains retard the reaction while larger ones tend to form more gaseous products.

2420. Kamiike, O., Kataoka, S., Nibayashi, M., and Negishi, R. Hydrocarbons From Carbide. II. Noncatalytic Polymerization Under Ordinary Pressure—Analysis and Liquid Products. Jour. Soc. Chem. Ind. (Japan), vol. 44, suppl. binding, 1941, p. 451 (in English); Chem. Abs., vol. 44, 1950, p. 8853.

Gaseous products were analyzed by the modified Schuftan method for CO_2, C_2H_2, C_2H_4, C_2H_{2n}(?), CO, O_2, H_2, N_2, and saturated gases. The liquids were analyzed chemically and were distilled into fractions, the molecular weight of such fractions being determined by the lowering of the freezing point of C_6H_6. A pilot plant yielded products very similar to those from the laboratory experiments. The liquid products were mainly aromatic and condensed aromatic hydrocarbons.

2421. Negishi, R., and Kamiike, O. Hydrocarbons From Carbide. III. Noncatalytic Polymerization Under Ordinary Pressure—Carbon Dioxide-Carbide Systems. Jour. Soc. Chem. Ind. (Japan), vol. 44, suppl. binding, 1941, p. 451 (in English); Chem. Abs., vol. 44, 1950, p. 8853.

Yield of liquid hydrocarbons is as high as 43.3% based on the C_2H_2, which reacts. The liquid products contain some oxygenated compounds and some evidence exists indicating that they are alcohols. The CO_2 reacts almost quantitatively with the CaO formed from the carbide and water vapor but not with that contained in the original carbide as an impurity.

2422. Negishi, R., Kamiike, O., and Kataoka, S. Hydrocabons From Carbide. IV. Noncatalytic Polymerization Under Ordinary Pressure—Carbon Monoxide–Carbide System and Hydrogen Chloride–Carbide Systems. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, p. 46; Chem. Abs., vol. 44, 1950, p. 10299.

These systems were investigated to determine if a typical Fischer-Tropsch reaction is effected with the carbide and its reaction products, but in the absence of the usual catalyst, to increase the total yield of liquid products and to learn the catalytic effect of HCl. The reaction between CO and H_2 occurred only to a slight extent in the range 150°–450°, resulting in no liquid products. The effect of HCl vapor was that, as the concentration of acid increased, the yield of liquid hydrocarbons decreased.

2423. Negishi, R., and Kamiike, O. Hydrocarbons From Carbide. V. Noncatalytic Polymerization Under Ordinary Pressure—Acetylene–Carbide Systems. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, p. 46 (in English); Chem. Abs., vol. 44, 1950, p. 10299.

Effects of C_2H_2 used as a carrier of water vapor on the liquid yield were studied in the hope that the total liquid yield might be increased by the polymerization of the introduced C_2H_2 and, further, that by its introduction, the formation of free C_2H_2 from the carbide might be suppressed, thus permitting the nascent C_2H_2 to become more readily available for the liquid synthesis. When the concentration of C_2H_2 was high, the total liquid yield also was high, showing that a part of the introduced C_2H_2 was polymerized. When its concentration was reduced, for example, by diluting it with H_2, or CO_2, the yield fell. In the presence of C_2H_2 mol., the formation of free C_2H_2 from the carbide is suppressed.

2424. ———. Hydrocarbons From Carbide. VI. Noncatalytic Polymerization Under Ordinary Pressure—Considerations and Comparisons Between Nascent and Ordinary Acetylene Polymerizations. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, p. 47 (in English); Chem. Abs., vol. 44, 1950, pp. 10299–10300.

Main reaction of nascent C_2H_2 is probably $nC_2H_2=C_{2n}H_{2n}$ to form principally aromatic and condensed aromatic compounds. The efficiency of the polymerization of nascent C_2H_2 from carbide is higher than that of ordinary C_2H_2 in the presence of an active catalyst. Because of the high reactivity of nascent C_2H_2, carbide may be used to accelerate certain sluggish reactions. Note should be made of the fact that the polymerization of nascent C_2H_2 is difficult to stop at a specfic point and that the heat of reaction involving carbide is very high.

2425. Negishi, R., Nibayashi, M., Sakon, K., and Kamiike, O. Hydrocarbons From Carbide—Noncatalytic Polymerization Under Elevated Pressure. I. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, p. 141; Chem. Abs., vol. 44, 1950, p. 8853.

Catalytic effect of the autoclave material in the synthesis of liquid hydrocarbons from carbide under elevated pressure is discussed. The autoclave reaction of CO and H_2 is reported to give (1) CH_4 and H_2O,

(2) C_2H_6 and H_2O, and (3) CO_2 and H_2. Reaction (3) is catalyzed by $Al(OH)_3$. No liquid hydrocarbon was formed when carbide was absent.

2426. Negishi, R., Nibayashi, M., and Kamiike, O. Hydrocarbons From Carbide; Noncatalytic Polymerization Under Elevated Pressure. II. Hydrogen–Carbide and Water Gas–Carbide Systems. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, suppl. binding, pp. 215–216 (in English); Chem. Abs., vol. 45, 1951, p. 535.

Yield of liquid product in the CaC_2–H_2–$Al(OH)_3$ system increases with increasing total pressure up to 100 kg./sq. cm. and then decreases. The amount of saturated gases increases with the total pressure. Decreasing the temperature increases the ratio of unsaturated to saturated compounds. Water gas in place of H_2 gives about the same yields of liquid products, and pressure has the same effect. The yield of saturated gases depends on the partial pressure of H_2. CO_2 in place of H_2 increases the yield of liquid product. The mechanism is discussed.

2427. Neidig, C. P. Formaldehyde Presents a Changing Economic Picture. Chem. Inds., vol. 61, 1947, pp. 214–217.

Formaldehyde production has tripled since 1939. In addition to an increase in the facilities for its manufacture by MeOH oxidation, production by direct oxidation of petroleum hydrocarbons continues to gain on a relative basis. From only 3 producers in 1937, the number has increased to 12 producers with 17 plants and 6 under construction. Eight plants use an Ag catalyst, at least 2 use an Fe–Mo oxide catalyst for the oxidation of MeOH. 2 plants use petroleum gases as the raw material and 1 will use a natural-gas cut. Little CH_2O is expected from the modified Fischer-Tropsch plants now being constructed. They will produce small quantities of MeOH, but, in the main, the oxygenated products will be C_2 and higher.

2428. Neil, D. J. Sheet Specimen Scanner for X-Ray Diffraction. Canadian Jour. Tech., vol. 29, No. 2, 1951, pp. 84–86.

An improved and simple design is described and illustrated. Simultaneous back reflection and transmission photographs at distances of 3 and 5 cm., respectively, and at any glancing angle from 0° to 90° are possible. The area scanned is approximately 2 cm.^{2} at rates of either 2 cm.^{3}/hr. or 4 cm.^{2}/hr. Useful exposures can be obtained with exposure times as low as 10 min.

2429. Nekrasov, P. [Substitutes for Petroleum in U. S. S. R.] Planovoe Khoz., 1939, No. 11, pp. 28–44; Khim. Referat. Zhur., 1940, No. 6, p. 106; Chem. Abs., vol. 36, 1942, p. 4994.

Motor fuel can be produced in U. S. S. R. by destructive hydrogenation of fuel, by semicoking of coals and shales, and by synthesis from gases. Benzene, alcohol, and gases can be used as motor fuel. Fuel suspensions and mixtures of coal with sulfurous fuel oil can be used in the metallurgical and the transportation industries.

Nelson, E. F. *See* abs. 776.

2430. Nelson, W. L. Fischer-Tropsch Process for Natural Gas. Oil Gas Jour., vol. 43, 1944, No. 12, p. 189.

An exact statement on the possibilities of the Fischer-Tropsch process is difficult at the present time because of the lack of knowledge of recent German developments. However, it is believed that much of the motor fuel being used by the Germans is made by synthesis from CO and H_2. Coal is the raw material rather than natural gas.

2431. Nemchinskiĭ, A. L. and Delle, V. A. [Carbide Formation During Carburization.] Metallurg., vol. 13, December 1938, pp. 55–60; Met. Abs. (in Metals and Alloys), vol. 10, No. 5, 1939, p. 278; Chem. Abs., vol. 33, 1939, p. 5783.

During carburizing of C steel with wood charcoal or with a mixture of wood charcoal (60%) and $BaCO_3$ (40%), the saturation of the steel with C is not limited by the *Acm* line of the Fe–C diagram but continues to the formation of carbides. The limit of saturation is less with C than with a mixture of C and $BaCO_3$. At higher temperatures of cementation the carbide formation is sometimes slower than at lower temperatures. This may be due to formation of a carbide network at high temperatures, which hinders the diffusion of the C into the austenite grains. Cr steel has a greater speed of carbide formation than plain C steel. The limit of saturation is higher for Cr–Ni than for C steel.

2432. Netter, J. [Methods for Study of Catalysts for Synthesis and Transformation of Hydrocarbons.] Mem. services chim. état (Paris), vol. 32, 1945, pp. 299–318; Fuel Abs., November 1948, abs. 3986.

Mechanism of contact catalysis, especially for the catalytic synthesis and transformation of hydrocarbons. Numerous diagrams and detailed description of equipment used.

Neumann, B. *See* abs. 3098.

2433. Neumann, B., and Biljcevic, P. [Catalytic Preparation of Formaldehyde.] Ztschr. angew. Chem., vol. 40, 1927, pp. 1469–1474; Chem. Abs., vol. 22, 1928, p. 760.

Theoretical considerations show that in CO_2–H_2 mixtures at equilibrium only traces of HCHO can be present. Only traces were produced in porcelain and SiO_2 tubes at varying temperatures without catalyst or with the following: Silica–gel, Ce_2O_3, V_2O_5, NaOH–CaO, $CuCl_2$, activated C and Cl_2, $CuCl_2$, on silica–gel, Pd sponge, hopcalite, Fe–Pd, Ni–Fe–Pd, Fe–Co, Mn–Co, and others.

2434. Neumann, B., and Jacob, K. [Equilibrium in Formation of Methane From Carbon Monoxide and Hydrogen, or From Carbon Dioxide and Hydrogen.] Ztschr. Elektrochem., vol. 30, 1924, pp. 557–576; Brennstoff-Chem., vol. 6, 1925, p. 197; Chem. Abs., vol. 19, 1925, p. 1083.

Correlated survey of equilibrium conditions for the formation of CH_4 by the reactions (1) $CO+3H_2\rightleftharpoons CH_4+H_2O$ and (2) $CO_2+4H_2\rightleftharpoons CH_4+2H_2O$ over the temperature range 300°–1,050°. The experimental determinations of the equilibrium were made by the dynamic method, highly purified gas mixtures being passed over a Ni catalyst. The catalyst was made by igniting $Ni(NO_3)_2$ that had been deposited on MgO granules. The supported NiO thus formed was reduced at about 280° by H_2. All experiments were at atmospheric pressure. The velocity of gas flow was in all cases 5 cm.^{3} per min. In experiments on reaction (1) the catalyst was 6.6 gm. Ni deposited on 45 gm. MgO. Reduction of CO to CH_4 began at 170°, was complete at 288°, and remained so up to 303°. Above 303° the CH_4 yield decreased regularly, until at 1,052° it had become zero. At temperatures above 389° the methanation reaction (1) is complicated by the secondary reactions $2CO\rightleftharpoons CO_2+C$, $CO+H_2O\rightleftharpoons CO_2+H_2$ and $CO_2+4H_2\rightleftharpoons CH_4+2H_2O$. In the temperature region 450°–780° all 4 reactions go on together. Above 780° the secondary reactions subside. In experiments on reaction (2) the same amount of catalyst was used. Reduction of CO_2 to CH_4 began slightly over 180° and reached a maximum at 328°, corresponding to a CH_4 yield of 95.3%. The CH_4 yield decreased above 328° and reached zero at 1,020°. Above 540° the reaction (2) is complicated by many secondary reactions. Among them are $C+CO_2\rightleftharpoons 2CO$, $CO_2+H_2\rightleftharpoons CO+H_2O$, $CO_2+Ni\rightleftharpoons NiO+CO$. In experiments on reaction (3) $CH_4+H_2O\rightleftharpoons CO+3H_2$ the catalyst was 1.6 gm. Ni deposited on 45 gm. MgO. The gas mixture was 43% CH_4 and 57% steam. No reaction was observed below 330°. From 330°–1,034° the amount of CH_4 undergoing reaction increased regularly. In the region 300°–860° the reaction is complicated by secondary reactions, as in the reverse reaction (1). Above 860° the reaction proceeds exclusively in accordance with the equilibrium reaction (3). Experiments on reaction (4) $CH_4+2H_2O\rightleftharpoons CO_2+4H_2$ from 320°–1,040° show plainly that, in spite of the presence of excess steam, the principal reaction is that corresponding to reaction (3). The observed values for the equilibruim constants $P\ \mathrm{CO}\times P^3\mathrm{H_2}/P\ \mathrm{CH_4}\times P\ \mathrm{H_2O}$ in the temperature region 860°–1,052°, agreed fairly well with those calculated by combination of the equilibruim constants for the 3 reactions $C+CO_2\rightleftharpoons 2CO$, $C+2H_2\rightleftharpoons CH_4$ and $CO_2+H_2\rightleftharpoons CO+H_2O$. The experimental results show somewhat better agreement with those calculated by means of "chemical constants" (Nernst). Agreement between the observed values for the equilibrium constants of reaction (2), $P\ \mathrm{CO_2}\times P^4\ \mathrm{H_2}/P\ \mathrm{CH_4}\times P^2\ \mathrm{H_2O}$, and those calculated by combining the equilibrium constants of the 3 reactions $C+CO_2\rightleftharpoons 2CO$, $C+2H_2\rightleftharpoons CH_4$ and $2(CO_2+H_2\rightleftharpoons CO+H_2O)$ was very poor.

2435. Neumann, B., and Köhler, G. [Equilibrium Relations in the Water-Gas Reaction in the Temperature Range 300°–1,000°]. Ztschr. Elektrochem., vol. 34, 1928, pp. 218–237; Chem. Abs., vol. 22, 1928, p. 2868.

Equilibrium values for the reaction, $CO+H_2O\rightleftharpoons CO_2+H_2$, were accurately determined at temperatures 300°–1,000° by a dynamic method. The catalyst used was Co oxide; this was replaced at the lower temperatures by Fe oxide in order to avoid the formation of CH_4. Small amounts of Al_2O_3 and KOH were present in the catalyst to increase its hardness and to act as a promoter. The values obtained for the equilibrium constant, $K=(CO)(H_2O)/(CO_2)(H_2)$, were reproducible and were virtually the same at each temperature regardless of the direction in which the equilibrium was approached. From the value $K_{800^\circ}=1.61$, a value slightly higher than that obtained by Hahn, the integration constant of the reaction isochore was found to be 0.84 and $\Delta H_o=9{,}500$ cal. The curve obtained from the isochore with these values agrees with the experimental data. The value of the integration constant also agrees with that obtained from vapor pressure data according to the Nernst heat theorem. The constants calculated by combination of the equilibria Fe–O–H and Fe–O–C, from the results of Eastman (abs. 762) and of Hofmann (abs. 1451) agree only partly with the observed values.

2436. Neumann, B., Kröger, C. and Fingas, E. [Water-Gas Generation From Coal and Coke.] Gas- u. Wasserfach, vol. 75, 1932, pp. 972–973, 973–974; Ztschr. Elektrochem., vol. 38, 1932, pp. 936–938; Chem. Abs., vol. 27, 1933, p. 827.

Polemical (abs. 713). The degree of attainment of the water-gas equilibrium depends more on the ash content of the given coke than on its reactivity. Dolch's conclusions also apply only to a limited temperature range. Dolch has not proved that CO_2 is not formed directly by the reaction of H_2O on C. Experiments with graphite showed that additions of Fe_2O_3, CuO, and K_2O all increased its reactivity but that only the 1st oxide permitted attainment of the water-gas equilibrium.

2437. Neumann, R. and Schroeder, W. C. Fischer-Tropsch Plant of Hoesch Benzin A.-G. at Dortmund, Germany. FIAT Rept. 239, 1945, 5 pp.; PB 1279, TOM Rept. 22, TAC Rept. SnMC–8, TOM Reel 199.

This plant employed the medium-pressure process using the normal Co–ThO_2–MgO–kieselguhr catalyst at about 10 atm. pressure and 180°–205° with synthesis gas of CO : H_2 ratio of 1:2 made from blue water gas. The catalyst chamber house contained 68 converters of the usual concentric double-tube design. They were operated in 3 stages: 1st 40 chambers, 2d 16–20, and 3d 4–8. Each stage was followed by indirect coolers and, following the final stage, gas pressure was reduced, and the C_3 and C_4 hydrocarbons were removed in the usual active C absorbers. There were no facilities for recycling the gas through any stage. The rate of feed of synthesis gas to the first stage was 1,000 m.^{3} per hr. per chamber. The gas contraction was 50–60% for the 1st stage, 35–40% for the 2d and 30% for the 3d. The average yield of primary product was 150 gm. per m.^{3} of synthesis gas or a total production of 50,000 ton per yr. The procedure of adding fresh catalyst in any stage instead of in the 3d stage only differs from the usual practice as recommended by Ruhrchemie. The regeneration of the catalyst with H_2 was claimed unsatisfactory and extraction with middle oil from the process was practiced instead. The catalyst gave only 1,500–2,000 hr. service when it was removed and shipped back to Ruhrchemie as spent catalyst. The products obtained from the primary product were approximately: Benzine 20–25% with 40–45 octane no., Diesel oil 30% with 100 cetane no., heavy oil 25%, paraffin 20–25% with melting point of 60°–70° and an initial boiling point of approximately 350°. Little research had ever been carried out at this plant.

2438. Neuwirth, F. [Production of Benzine From Coal.] Sparwirtschaft, vol. 15, 1937, pp. 129–134; Chem. Abs., vol. 31, 1937, p. 5538.

Review dealing mainly with hydrogenation of coal and the Fischer-Tropsch process.

2439. ———. [Benzine From Coal.] Österr. Chem.-Ztg., vol. 41, 1938, pp. 75–82; Chem. Abs., vol. 32, 1938, p. 3127.

Processes for the production of gasoline by low-temperature carbonization of brown coals, the hydrogenation of tar or coal, and synthesis of water gas are outlined.

2440. ———. [New Coal-Utilization Methods.] Österr. Ing. Architekt. Ver., vol. 90, 1938, pp. 196–201; Chem. Abs., vol. 33, 1939, p. 835.

Summary of new developments in coking, burning, gasification, hydrogenation and pressure-extraction of coal. Fischer-Tropsch and other processes are described.

Neville, H. A. *See* abs. 3340.

Newall, H. E. *See* abs. 450.

2441. Newey, H. A., Shokal, E. C., Mueller, A. C., Bradley, T. F., and Fetterly, L. C. Drying Oils and Resins—Segregation of Fatty Acids and Their Derivatives by Extractive Crystallization With Urea. Ind. Eng. Chem., vol. 42, 1950, pp. 2538–2541; Chem. Abs., vol. 45, 1951, p. 2230.

When a mixture of fat acids or their derivatives (Me esters, alcohols, nitriles) is allowed to react with urea, with or without solvent, the more saturated components form insoluble adducts. A stereochemical explanation is given. Thus 250 gm. linseed-oil fat acids (I No. 180) in 250 gm. MeCOCHMeEt is mixed with 2 l. of saturated aqueous urea, the resulting precipitate filtered off and decomposed with H_2O, yielding 16% of a fraction of I No. 54. Glyceride oils did not form precipitates. Numerical data on the segregation of various fat acids and derivatives are given. 25 refs.

2442. ———. Separation of Fatty Acids and Their Derivatives by Extractive Crystallization With Urea. Am. Paint Jour., vol. 34, May 1, 1950, pp. 76–78; Chem. Zentralb., 1951, I, p. 1662.

When fatty acids are mixed with saturated, aqueous, or alcoholic solutions of urea, the more-saturated components form complex insoluble compounds which can be separated by filtration. There remains behind a raffinate of high I number. The method is cheap, operable at room temperature, and useful for separating the alcohols and nitriles of fatty acids.

2443. Newitt, D. M. Design of High-Pressure Plant and the Properties of Fluids at High Pressures. Oxford University Press, London, 1940, 491 pp.

———. *See* abs. 3028.

2444. Newitt, D. M., and Gardner, J. B. Initial Formation of Alcohols During the Slow Combustion of Methane and Ethane at Atmospheric Pressure. Proc. Roy. Soc., vol. 154, A, 1936, pp. 329–335; Chem. Abs., vol. 30, 1936, p. 4461.

By removing and analyzing the products formed by the surface reactions during the induction periods of the slow combustion of CH_4 and C_2H_6, it was found that MeOH and EtOH were formed in quantities comparable with those of the corresponding aldehydes, the alcohol: aldehyde ratio diminishing, however, as the induction approached completion. It was also proved that the formation of the alcohols preceded that of the aldehydes.

2445. Newitt, D. M., and Haffner, A. E. Formation of Methanol and Formaldehyde in the Slow Combustion of Methane at High Pressures. Proc. Roy. Soc. (London), vol. 134, A, 1932, pp. 591–604; Chem. Abs., vol 26, 1932, p. 2697.

In the slow combustion of CH_4 at high pressures, considerable quantities of the primary product, MeOH, survive and can be isolated. As combustion proceeds in an 8:1 CH_4+O_2 mixture, the rate of formation of MeOH increases with the $CH_4:O_2$ ratio until a point is reached when the concentration of steam and CO in the products begin to exert a retarding effect. At any particular pressure there is a definite temperature at which optimum amounts of MeOH and HCHO survive. The effect of increasing pressure is not only to increase the amounts of both products surviving, but also to increase the ratio MeOH: HCHO. The oxidation of CH_4, under the experimental conditions described is mainly a surface effect and is characterized by a marked induction period.

2446. Newitt, D. M., and Momen, S. A. Synthesis of Aliphatic Acids by Interaction of Olefins With Carbon Monoxide and Steam and Related Reactions. Jour. Chem. Soc., 1949, pp. 2945–2948.

It is shown that C_2H_4 and CO, in the presence of a suitable catalyst and at temperatures of 250° and upward, can unite with neutral or basic molecules, such as H_2O, EtOH, benzyl alcohol, NH_3, and aniline, to give acids, esters and amines. The synthesis of propionic acid by this reaction has been studied at 150–400 atm. and 250°–330°. The yield of acid in the products depends on the relative rates of its formation and thermal decomposition and also on the extent to which CO undergoes decomposition to CO_2.

2447. Newitt, D. M., and Szego, P. Slow Oxidations at High Pressures. I. Methane and Ethane. II. Methanol, Ethyl Alcohol, Acetaldehyde, and Acetic Acid. Proc. Roy. Soc. (London), vol. 147, A, 1934, pp. 555–571; Chem. Abs., vol. 29, 1935, p. 1770.

Large amounts of MeOH (EtOH) are formed in the early stage of the slow oxidation of CH_4 (C_2H_6) at 50 atm. Under similar conditions, the products obtained from EtOH, MeOH, AcH, and AcOH are such as to indicate a hydroxylation mechanism of combustion. The oxidation of AcOH at reduced pressures (in silica) is predominantly homogeneous. At 426°–486° at 200 mm. there is no marked induction period. The products are CO, CO_2, CH_4, and H_2O, with traces of AcOMe and acetone.

2448. Newitt, D. M., Byrne, B. J., and Strong, H. W. Equilibrium in the System: Methanol–Hydrogen–Carbonic Oxide. Proc. Roy. Soc. (London), vol. 123, A, 1929, pp. 236–252; British Chem. Abs., 1929, A, p. 508; Chem. Abs., vol. 23, 1929, p. 3148.

Equilibrium in the system CH_3OH–H_2–CO was approached from both sides by static and dynamic methods. Total pressures of the order of 100 atm. were measured by movement of a disk observed by optical methods. The composition at equilibrium was determined by gas analysis. Partial pressures were calculated assuming no deviation from Boyle's law. The results from 260°–380° are not in agreement with prediction for the equilibrium position made by Kelley or by Audibert and Raineau. The free-energy equation derived from the measurements is $\Delta F=70.5T-30{,}500$.

2249. Newman, L. L. Thyssen-Galocsy Slagging Gas Producer. CIOS Rept. XXIX–51, 1945, TOM Reel 198, Solid Fuels Rept. 46, PB 955.

Report of the operation of a Thyssen-Galocsy slagging gas producer of 40 ton per day gasifying capacity at the Wanne-Eickel plant of the Krupp Treibstoffwerk. The purpose was to demonstrate the feasibility of gasifying any grade of fuel in any size or combination of sizes 5–80 mm., coking or noncoking, regardless of the ash-fusing temperature. The generator was shaped like a blast furnace, 35 ft. high and 10 ft. in diameter, 3 levels of tuyères with 5 tuyères at each level, those of the lowest level being water-cooled and burning gas from the producer itself, or any other source in a mixture of O_2 and steam and admitted into the fuel bed at a temperature high enough to cause the steam and CO_2 to react with the C. The tuyères at the upper levels admit additional O_2 to supply heat to balance the amount required for the reduction of the steam and CO_2 and to melt the ash. Only 1 of the 2 upper levels is used at a time. The slag is removed through a tap hole 650 mm. above the bottom of the shaft, which is lined to a height of 1 m. with slag resistant refractory. A temperature of 1,600° in the fuel bed was found necessary for trouble-free operation. O_2 for the operation was supplied by the Hibernia Stickstoffwerk, but it was thought that cheap O_2 (1–2 pf. per $m.^3$) could be produced by using coal screenings to generate steam at high pressure for driving the turbo-blowers and compressors in the Linde-Fränkl plant and by using the exhaust steam in the gasification process. The results of 1 day of a typical 3-day test are presented: O_2, 90% pure, consumed 25,000 $m.^3$, steam 18.9 tons, auxiliary gas, produced in the process, 17,250 $m.^3$, coke, 40–60 min. diam., ash 8.5%, 6,865 kcal. per kg., 41.3 tons: yields of gas, less auxiliary gas, 89,270 $m.^3$, analysis CO_2 2.1, O_2 0.1, CO 71.0, H_2 23.3, CH_4 0.2 and N_2 3.3%, 2,760 cal. per $m.^3$, steam decomposition 90.1%, gasification 86.7%, requirements for each cubic meter of oxygas, 0.29 $m.^3$ O_2, 0.21 kg. steam and 0.46 kg. coke. It is not considered that these tests have reached the peak of capacity of the unit, but that higher results will be attained when unlimited supplies of O_2 are available.

2450. Newman, L. L. Oxygen Gasification Processes in Germany. Coal Technology, vol. 1, 1946; Am. Inst. Min. and Met. Eng., Tech. Pub. 2116, 1946, 16 pp.; Chem. Abs., vol. 41, 1947, p. 1079.

Review and digest of recent CIOS reports on gasification processes under 4 headings: Processes (1) in which fine fuel is gasified in a fluidized bed (example, the Winkler process); (2) in which fine fuel is gasified in suspension (example, Koppers and Schmalfeldt processes); (3) in which fine fuel is gasified in a fixed bed (example, the Lurgi process); (4) in which lump fuel is gasified in a fixed bed (example, the Thyssen-Galocsy slagging generator and the Leuna slagging generator). Typical operating data are given for each process, and diagrams of the plants are shown. The economics of O_2 production by the Linde-Fränkl process is presented. It is stated that power requirements in Germany for producing O_2 of 98% purity were about 12 kw.-hr. per 1,000 cu. ft. and that in plants of 75,000 cu. ft. per hr., capacity the cost of power was 50% of the total cost, amortization and interest 40%, and labor and materials 10%. If the same relations between power costs and other costs should prevail in America, O_2 of 98% purity should be obtainable for $0.12 per 1,000 cu. ft. with power at $0.005 per kw-hr.

2451. ———. Oxygen Production, Utilization in Gas-making Processes. Proc. Am. Gas Assoc., vol. 28, 1946, pp. 444–467.

Review of the methods of O_2 manufacture and coal gasification.

2452. ———. Oxygen Production, Utilization in Gas-making Processes. Gas, vol. 22, No. 12, 1946, pp. 43–44.

Digest of a paper presented at the American Gas Association convention, October 1946. The use of O_2 in place of air in a gas producer makes the problem of complete gasification relatively simple. A survey of manufacturers of large-scale O_2 plants has put the cost of O_2 at about $0.14–$0.18 per 1,000 cu. ft. Several processes have been developed for the utilization of O_2 in gas making: Those with the fixed-fluidized beds such as the Winkler, the O_2 requirements of which are high; the powdered-fuel types with fuel in suspension which promise economy in fuel and O_2 consumption and adaptability to any suitably grindable coal; the fixed-fuel-bed types with mechanical grates and high pressures; the pressure types which have a high capital cost and a high fuel and steam consumption and require a noncaking coal. In general local conditions of fuel, labor and power costs will determine which process is most likely to succeed. The high investment cost of O_2 plant will make the production of gas by the use of O_2 economical only as a base-load proposition.

2453. ———. Synthetic Oil. Federal Sci. Progress, vol. 1, 1947, pp. 11–13.

Nontechnical exposition of American progress in the development and utilization of the Fischer-Tropsch process for producing liquid fuels from coal and natural gas. Simplified flowsheet is included.

2454. ———. Use of Oxygen in the Production of Hydrogen or Synthesis Gas. Ind. Eng. Chem., vol. 40, 1948, pp. 559–582; Chem. Abs., vol. 42, 1948, p. 4329.

Processes for the large-scale production of H_2 and synthesis gas are basically identical, and the cost of these gases represents a major item of expense in the production of liquid fuels by the Bergius and Fischer-Tropsch methods. To produce only 25,000 bbl. of primary liquid fuels by the Fiscrer-Tropsch process 700,000,000–800,000,000 cu. ft. of synthesis gas would be required. To produce these huge volumes of synthesis gas, high-capacity processes must be employed, and the low-priced generator fuels are required in order to make the process economical. These can best be gasified in continuous, internally heated processes using O_2. The principal processes for this include 4 types: Winkler, gasifying fines in a fixed fluidized bed; Koppers, gasifying pulverized coal in suspension; Lurgi, gasifying fines in a fixed bed under pressure; Thyssen-Galocsy and Leuna, gasifying lump fuel and disposing of the ash as a molten slag. Each of these processes, their operating characteristics and economic status are discussed thoroughly. Other less-important processes are briefly described: Fuel Research Board vortex chamber, gasifying pulverized coal in a rotating, porous fuel bed; Wintershall-Schmalfeldt, gasifying coarse brown coal with circulating gas and steam; and Metallgesellschaft dust-gasification process, gasifying coal dust with recirculation of hot gases. It is concluded that American requirements may be best satisfied by gasification processes using pulverized fuel in suspension. These will permit the use of higher rank caking or noncaking coals, as well as the lower-rank subbituminous coals or lignite.

———. *See* abs. 1468, 3743.

2455. Newman, L. L., Schmidt, L. D., and Batchelder, H. R. Manufacture of Fuel and Synthesis Gas in the United States. Trans. World Power Conf., 4th Conf., London, Sec. D–1, Paper 5, 1950, 12 pp.; Chem. Abs., vol. 44, 1950, p. 7039.

Use of gas in the United States is increasing steadily, but most of it is natural gas, owing to the increasing cost of materials for gas manufacture. Production of chemicals consumes large amounts of gas and the production of synthetic liquid fuels is on the verge of realization. Increasing quantities of gas will have to come from coal. New technical developments in commercial gas manufacture include conversion of water-gas generators to oil-gas operation, and reforming processes for liquefied petroleum gases and other hydrocarbons. O_2 is being applied commercially for synthesis-gas production from coke, and investigations are under way relative to the use of O_2 for the pressure gasification of lump coal and for the gasification of granular or pulverized coal.

2456. Newton, R. H., and Dodge, B. F. Equilibrium Among Carbon Monoxide, Hydrogen, Formaldehyde, and Methanol. I. The Reactions $CO+H_2\rightleftharpoons HCHO$ and $H_2+HCHO\rightleftharpoons CH_3OH$. Jour. Am. Chem. Soc., vol. 55, 1933, pp. 4747–4759; Chem. Abs., vol. 28, 1934, p. 955.

Trace of CH_2O is synthesized from CO and H_2 over a Cu–Zn catalyst at 225°–250° and 3 atm.; the equilibrium approached from both sides gives $\log K_p=(374/T)-5.431$ approximately. CH_2O is readily hydrogenated at 120°–200° and 1 atm. over various Cu-alloy and other catalysts, but Os, Pt and pure Zn are inactive: $\log K_p=(4{,}600/T)-6.470$ approximately. A change in the composition or structure of the catalyst has a marked effect on the nature and amount of side reaction, Ni catalysts promoting decomposition of CH_2O, while some Cu catalysts yield 53–72% HCO_2Me. Conclusion: Direct thermal synthesis of CH_2O is not feasible; its production from MeOH requires a temperature of 400°.

2457. ———. Equilibrium Among Carbon Monoxide, Hydrogen, Formaldehyde, and Methanol. II. The Reaction $CO+2H_2\rightleftharpoons CH_3OH$. Jour. Am. Chem. Soc., vol. 56, 1934, pp. 1287–1291; Chem. Abs., vol. 28, 1934, p. 4651.

Uncertainty in the heat data for CO and MeOH permits several possible theoretical equations for the synthesis of MeOH from CO and H_2. The equation $\log Kp_0=(3724/T)-9.1293 \log T+0.00308\,T+13.412$ fits results obtained at 225°, 250°, and 275° and 3 atm. for 4–55 hr. over a Cu–Zn catalyst.

2458. ———. Activity Coefficients of Gases. Application to Calculation of Effect of Pressure on Homogeneous Chemical Equilibria and to Calculation of Integral Joule-Thomson Effects. Ind. Eng. Chem., vol. 27, 1935, pp. 577–581; Chem. Abs., vol. 29, 1935, p. 3900.

Use of Newton's curves of activity coefficients in calculating chemical equilibrium constants is illustrated by application to the synthesis of NH_3 and of MeOH. A simple approximate method of calculating the temperature drop on isenthalpic expansion of a gas is given; specific-heat data and the activity coefficients are used. The results of both types of calculation are compared with experimental data.

Newton, W. L. *See* abs. 855.

Nibayashi, M. *See* abs. 2419, 2420, 2425, 2426.

2459. Nicholson, E. W., Moise, J. E., and Hardy R. L. Fluidized-Solids Pilot Plants. Ind. Eng. Chem., vol.

40, 1948, pp. 2033–2039; Chem. Abs., vol. 43, 1949, p. 1613.

Main commercial application to date of the fluidized-solids technique has been in the field of catalytic cracking of petroleum oils. Due to its extreme flexibility and versatility it will undoubtedly be applied to an increasing number of processes. The technique is particularly adaptable to mixed-phase (solid-gas) processes requiring the addition or removal of large amounts of heat, especially where isothermal conditions are desirable. The fluidized solids may be catalysts, reactants, inert heat-transfer mediums, or adsorbents. One of the most interesting new developments is in the field of hydrocarbon synthesis and commercial plants employing this fluid technique are being planned. The steps necessary for the practical design of a pilot plant utilizing the fluidized solids technique are presented. An apparatus which has been used for fluidization studies essential to unit design is illustrated. The translation of data obtained in such equipment to the design of reaction vessels, circulating equipment, gas and solids inlet distributors, solids recovery, etc., is outlined. Methods of measurement and control of temperature, pressure, solids flow rate and space velocity are discussed.

2460. Nicolai, J., d'Hont, M., and Jungers, J. C. [Synthesis of Methane From Carbon Dioxide and Hydrogen Over Nickel.] Bull. soc. chim. belg., vol. 55, 1946, pp. 160–176; Chem. Abs., vol. 41, 1947, p. 4699.

Kinetics are compared for the hydrogenation of CO and CO_2 over Ni in the pressure range 0.1–1 atm. and temperature range 180°–300°. Kinetics of the CO–H_2 reaction indicate that H_2 is feebly adsorbed, CO strongly adsorbed by Ni. The velocity is not significantly affected by the presence of the products. Reaction is more rapid when D_2 is used in place of H_2. Kinetics of the CO_2–H_2 reaction indicate that both reactants are weakly adsorbed, the products retard the reaction and D_2 behaves exactly like H_2. Hydrogenation of CO is slower and has a higher activation energy than that of CO_2. When a mixture of CO and CO_2 is hydrogenated, the CO, very strongly adsorbed, reacts completely first, the CO_2 then reacts more rapidly.

2461. Nicolaï, J., Martin, R., and Jungers, J. C. [Kinetics of the Hydrogenation of Benzene.] Bull. soc. chim. belg., vol. 57, 1948, pp. 555–574; Chem. Abs., vol. 44, 1950, p. 419.

The reaction cyclohexane$+$CO$=$benzene$+CH_4+H_2O$ is thermodynamically favorable but does not go well over Ni. Since CO is readily hydrogenated, it was desired to observe the dehydrogenation of cyclohexane (I), but this is limited by equilibrium at some of the temperatures of interest, so the reverse reaction of hydrogenation of benzene (II) was studied at 60°–330°. The catalyst was prepared by reduction of $NiCO_3$ deposited on kieselguhr. Data obtained in a static system are presented in curves. At 70°–150° the hydrogenation produces (I) and has an activation energy of (II) kcal. At 150°–250° it is complex. Above 250° the product is CH_4 (III) and the activation energy is 45 kcal. Thus at low temperatures there is an additive adsorption of (II), whereas at high temperatures there is a dissociative adsorption to products that are hydrogenated to (III). The orders of reaction in H_2 and (II) are fractional, about 0.5 in the low-temperature region. In the region of formation of (III) the order is first in (II) and negative in H_2. When (I) is treated in H_2 at 260° there is first dehydrogenation to (II) and then production of (III). The hydrogenation of (II) in the presence of various gases was observed; (I) did not inhibit at low temperatures, and (III) did not inhibit at high temperatures. The adsorption of CO was stronger than that of (II), and CO was hydrogenated first. Adsorption of CO_2 was about the same as that of (II). MeOH was not strongly adsorbed and below 160° had no effect, whereas at high temperatures it was decomposed and then converted to (III). The hydrogenation of mixtures of CO and (I) at 250°–280° showed first hydrogenation of CO, then dehydrogenation of (I) to (II), then conversion of (II) to (III). Thus CO does not aid in the dehydrogenation, for it is adsorbed more strongly and is hydrogenated first. The effect of CO_2 is similar though less marked. In mixtures containing CO, (I), and MeOH at 250° the first reaction was decomposition of the MeOH. Failure of the desired transfer of H_2 from (I) to CO is caused by 2 effects. First at temperatures above 180° where CO can be converted to (III), (II) formed is destructively adsorbed and the catalyst activity is lowered by carbonization unless much H_2 is present. Second, CO is preferentialliy adsorbed and keeps (I) from the catalyst.

2462. Nielsen, H. Oil From Coal. Gas. Jour., vol. 174, 1926, pp. 591–592, 650–653, 732–734; Chem. Abs., vol. 21, 1927, p. 2371.

Processes of low-temperature carbonization, the Bergius process, and Fischer's Synthol process are compared from the point of view of the economic conversion of coal into oil. Emphasis is laid on the importance of producing a primary oil by low-temperature carbonization. The Fischer-Tropsch Synthol process (abs. 1015) is discussed, and it is concluded that the most efficient method at present available for conversion of coal into oils consists in (*a*) low-temperature carbonization in the Laing and Nielsen retort, and (*b*) use of the coke as a source of water-gas and conversion of the latter into Synthol.

2463. Nienburg, —. [Transformation of a Synthetic Olefin Into Oxo-Alcohols.] FIAT Reel R–20, frames 7571–7580, Dec. 30, 1941; PB 73.564.

Report from the I. G. Farbenindustrie Ammonia Laboratory, Oppau, deals with tests on conversion of synthetic olefins into Oxo-alcohols and on separation of these from unsaponifiable matter by the boric acid ester method. Separation and fractionation proved to be difficult and incomplete. The essential result is that 30% of the olefins and the alcohols derived from them show a branched structure. Numerous tables are presented.

2464. ———. [Cracking of High Molecular Paraffin and Oxidation Gatsch.] FIAT Reel R–20, frames 7600–7614, Mar. 9, 1942; PB 73,564.

Differences between corresponding fractions of oxidation products obtained either from high-molecular paraffin or from medium-pressure paraffins are discussed and shown in tables. The fraction derived from the high-molecular paraffin is considerably inferior. It is thought that structural change, such as cyclization, occurs which is inherent in the material itself or which takes place during the cracking process.

2465. Nienburg, H. J. [Work on the Oxo Reaction 1940–1944.] BIOS Misc. Rept. (in German) 113, 1947, Appendix II, 16 pp; BIOS Final Rept. 1646, 1946, pp. 30–47, PB 91,685.

Changes in constitution brought about by the Oxo reaction were examined with pure olefins such as cetene and dodecylene. Independent of the purity of the initial olefin, a large number of isomeric Oxo alcohols or acids were obtained. Special Oxo reactions were carried out with olefins from first-running ketones, Fischer-Tropsch synthesis olefins, di- and tri-isobutylene, cracking olefins and with unsaturated, O-containing olefins. The latter did not yield uniform Oxo products. By treating olefins with NH_3 and CO acid amides were obtained. With isobutylene and generally, with all olefins having the double bond between tertiary and quaternary C atoms, it was found that the formyl grouping goes solely to the tertiary C atom. Work was done on building up high knock-rating hydrocarbons, using the Oxo reaction and starting with isobutylene, trimethylethylene, 2,4-dimethylpentene-2, diisobutylene and tetramethylethylene. It was found that these compounds avoid an increase in branching by a double-bond shift which precedes addition. In contrast to the Oxo reaction, 1,3-dioxanes give with tetramethylethylene, trimethylethylene and 2,4-dimethylpentene-2, the desired highly branched primary alcohols after hydrogenation. The oxation of propylene was intensively studied in a trickle (Riesel) apparatus, and a sump-phase apparatus was developed to handle 5 l. liquid propylene/hr. Propylene yielded equal quantities of normal- and isobutyl-aldehyde and the corresponding alcohols on hydrogenation.

Nierhaus, H. *See* abs. 2043.

2466. Niiranen, W. [Gasification of Wood and Peat With Special Reference to the Preparation of Synthesis Gas.] Suomen Kemistilehti, vol. 10, 1937, A, pp. 37–40; British Chem. Abs., 1937, B, p. 515.

Destructive distillation of dried wood shavings at 540° gives a large amount of tarry matter. This can be eliminated and more volatile hydrocarbons obtained by passing O_2 into the retort, the oxidation being adjusted to give the maximum CO : H_2 ratio for conversion into Kogasin.

2467. ———. [Synthesis of Liquid Fuels and Lubricating Oils.] Suomen Kemistilehti, vol. 10, A, 1937, pp. 7–9; Chem. Abs., vol. 31, 1937, p. 2773.

Brief survey.

2468. Nikitin, N. I. [Absorption of Hydrogen and Carbon Dioxide by Pyrophoric Iron, Nickel, and Cobalt.] Jour. Russian Phys.-Chem. Soc., vol. 58, 1926, pp. 1081–1094; Chem. Abs., vol. 22, 1928, p. 8.

Finely divided Fe, obtained by the action of H_2 on the carbonate at 515°–525°, adsorbed H_2 at −185° according to the equation $a=\beta p^{1/n}$. No adsorption was observed at −80° and +16°, while at 330° the gas diffuses through Fe. The adsorption isotherm of Ni at 19° is parallel to the axis of pressures showing compound formation. No combination occurs at −185°, since the corresponding isotherm begins at the origin. The 336° curve crosses that for 19°; its lower portion represents the dissociation of the Ni and H_2 compound. The above equation holds for Fe and CO_2 at 18° ($1/n=0.207$). Readsorption, after evacuating the system at 500°, was much smaller although similarly represented by a straight line; a slow reaction occurs at 500°. Ni adsorbs little CO_2 at 14° and 335°; the gas is only partly recovered by evacuation. Erratic results were obtained with Co prepared at 340°. A sample reduced at 525°–550° exhibited a continuous adsorption isotherm for CO_2 at 14°. Co lies between Ni and Fe as an adsorbent of CO_2.

2469. ———. [Hydrogen and Carbon Dioxide Absorption by Pyrophoric Iron, Nickel, and Cobalt.] Ztschr. anorg. Chem., vol. 154, 1926, pp. 130–143; Chem. Abs., vol. 20, 1926, p. 3255.

Experiments were carried out to determine the adsorption and solution of H_2 and CO_2 by pyrophoric Fe, Ni, and Co at different temperatures and pressures. A specially constructed apparatus for this is illustrated and described. Finely divided metals were obtained on slow reduction, in about 30 hr., of the respective carbonates with H_2, the reduction temperature being kept at 525° for Fe and at 350° for Ni and Co. The following results were obtained: For 5 gm. Fe the maximum H_2 adsorption at −185° and 667 mm. pressure was 8.3 cc. At −80° and 16° there was virtually no adsorption, while at 380° and 500° there was again a larger adsorption. The results obtained at different pressures exhibited in isotherms show an adsorption curve at −185°, following Freundlich's equation: $a=\beta p^{1/n}$, where β and $^{1}/_{n}$ are determined constants. A proof for the application of this equation is the straight line obtained on plotting log a against log p, the tangent to the angle between this end and X–axis being $^{1}/_{n}$. That surface adsorption and not solution occurred at −185° was proved by the easy removal of the H_2 on evaluation, while the H_2 taken up at 400° could be removed only by heating strongly. The results obtained with Ni and H_2 at −185°, 19° and 336° showed a maximum adsorption at 336°, which was 3.8 cm.³ for 5 gm. Ni at 714.9 mm. pressure. The isotherm for 19° exhibits a straight line parallel to the X–axis and points to the formation of a superficial layer of Ni–H. A similar formation is not present at −185° inasmuch as the isotherm starts at the O–point of the coordinate axis. The isotherm for 336° starts below that of 19°, because the loose Ni–H compound dissociates at higher temperature and lower pressure. Fe had a strong tendency to adsorb CO_2, 1 vol. Fe taking up 35 vol. CO_2 at ordinary temperature and pressure and 2 times as much at −80°. Ni adsorbed virtually no CO_2 at 335°. The application of Freundlich's equation for the CO_2 adsorption by Ni at lower temperatures was not safe because of the small values obtained. The results with Co and H_2 were all uncertain. Adsorption values for CO_2 and Co were found between those for Fe and Ni. 5 gm. Co adsorbed 13 cm.³ CO_2 at 14° and 760 mm. pressure.

2470. Nikitin, N. I., and Sharkov, V. I. [Adsorption of Gases by Finely Disintegrated Metals.] Jour. Russian Phys.-Chem. Soc., vol. 58, 1926, pp. 1095–1100; Chem. Abs., vol. 22, 1928, p. 1074.

Adsorption of H_2, CO_2 and NH_3 gases was investigated. The following powders were used: Cu, Pb, Fe, Co, Ni, Ni–Al_2O_3 mixture and Ag. Pb and Cu powders were obtained by reducing the basic compounds. Ag was obtained from the silver gel, which was dried in vacuum. Virtually no adsorption could be noticed with Pb or Cu powders; this is probably due to recrystillation of metals during the process of reduction. Ag adsorbed only a small amount of H_2, considerably more of CO_2. 5.512 gm. adsorbed 13.9 cc. of CO_2 (converted to 760 mm. and 0°) at −81°. Pyrophoric Fe adsorbed 11.5 cc. NH_3 at 97° and 158.6 mm. and 53.7 cc. at −18.2° and 556 mm. No adsorption occurred at higher temperature. Co adsorbs 10 times less than Fe. Ni powder did not adsorb any gases except when mixed with Al_2O_3. A mixture of 82.4% Ni and 17.6% Al_2O_3 was able to adsorb gases. 4.454 gm. adsorbed at 15°, 760 mm., 190 cc. NH_3; at −18.2°, 760 mm., 281 cc. After heating and applying vacuum, this mixture was freed from NH_3, gas and used again for the adsorption of CO_2. At 15° and 760 mm. 15.9 cc. CO_2 gas was adsorbed. Al_2O_3 without Ni, 4.6338 gm., adsorbed at 15° and 760 mm., 168 cc. gas. H_2 was not adsorbed by Al_2O_3.

2471. Nikitin, V. M. [Effect of the Conditions of Synthesis on the Quality of Methanol.] Jour. Chem. Ind. (U. S. S. R.), vol. 12, 1935, pp. 1233–1236; British Chem. Abs., 1936, B, p. 404; Chem. Abs., vol. 30, 1936, p. 2170.

Catalysts containing more Cr than $8ZnO\cdot1.2Cr_2O_3$ give larger amounts of byproducts in synthetic MeOH. The quantity of H_2O and higher molecular compounds formed is increased as the temperature is raised. When the rate of passing the gases over the catalyst is increased, the formation of aldehydes, ketones, and esters decreases more rapidly than that of acids. If the ratio of H_2 : CO is not 2, more byproducts are formed. Inert gases act as diluents and lower the quality of the MeOH.

2472. ———. [Byproducts of Methanol Synthesis.] Org. Chem. Ind. (U. S. S. R.), vol. 2, 1936, pp. 382–387; Chem. Abs., vol. 31, 1937, p. 1759.

Study of the properties of all combinations of binary systems of iso-BuOH, iso-BuOAc and H_2O includes mutual solubilities at various temperatures, equilibrium of liquid and vapor phases, azeotropic mixtures, density and *n*. The experimental results are tabulated, graphed and discussed. With increasing temperature the solubility of iso-BuOH in H_2O decreases and that of H_2O in iso-BuOH increases. The azeotropic mixture is composed of 68 mol. % of H_2O and 32 mol. % of iso-BuOH.

2473. ———. [Byproducts of Methanol Synthesis. II.] Org. Chem. Ind. (U. S. S. R.), vol. 3, 1937, p. 364; Chem. Abs., vol. 31, 1937, p. 7040.

Boiling points of mixtures of PrOH with H_2O are tabulated and graphed.

2474. ———. [Treatment of the Byproducts From the Methanol Synthesis. III.] Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 993–996; Chem. Abs., vol. 32, 1938, p. 1647.

Isobutyl acetate prepared from the iso-BuOH in synthetic MeOH can be dried by neutralizing with Na_2CO_3 and distilling into a continuous separator, or dried over $CaSO_4$. The higher-boiling oil from the MeOH is best dried by salting out the NaCl and drying over CaO or $CaSO_4$.

2475. ———. [Paper of D. A. Pospekhov on the Role of Copper in Methanol Catalysts.] Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 1229–1230; Chem. Abs., vol. 32, 1938, p. 911.

Criticism of Pospekhov's paper (abs. 2724).

2476. ———. [Purification of Crude Synthetic Methanol by Oxidizers.] Jour. Chem. Ind. (U. S. S. R.), vol. 14, 1937, pp. 1067–1072; Chem. Abs., vol. 32, 1938, p. 484.

Addition of $KMnO_4$ to crude MeOH and rectification to 75° gives a pure distillate. $CaOCl_2$ and $K_2Cr_2O_7$ are not quite as satisfactory oxidizers. Fe and Cu in the crude alcohol increase the rate of oxidation of impurities.

———. *See* abs. 892.

Nillson, K. T. *See* abs. 186.

Nishibayashi, Y. *See* abs. 2205.

Nishio, A. *See* abs. 1873, 3468.

Nishiyama, Z. *See* abs. 1484.

2477. Nissan, A. H. Thermal Catalysis of Carbon Monoxide and Hydrogen to Produce Hydrocarbons and Oxygenated Organic Compounds. Oil Gas Jour., vol. 37, No. 10, 1938, pp. 49–50, 55; No. 11, 1938, pp. 89–90, 93, 96; Chem. Ind., vol. 43, 1939, pp. 281, 283, 284; Chem. Abs., vol. 33, 1939, p. 7525.

Discusses economic value and technical applications of the hydrocarbons and oxygenated compounds formed. Reviews various reactions by which CH_4, MeOH and higher alcohols can be obtained. Fundamental thermodynamic and catalytic conditions for the production of hydrocarbons are dealt with in some detail and the conditions necessary for their successful technical synthesis are reviewed. Examples of the properties of the products are given, and the erection of commercial-scale plants is discussed from the economic viewpoint.

Nissen, B. H. *See* abs. 5.

2477a. Nistler, F. [New Methods for Producer-Gas Generation From Bituminous Coal.] Glückauf, vol. 88, 1952, pp. 346–349; Chem. Abs., vol. 46, 1952, p. 7,736.

Special slagging-gas producer for manufacturing a cheap gas from coal dust is described. The gas is similar to blast-furnace gas with a gross heating value of about 1,051 kcal. per m.³. This producer should be well adapted for use with a steam–O_2 mixture for generation of synthesis gas.

2478. Nitzschmann, R. [Oxidation of Carbon Monoxide by Steam.] Metallbörse, vol. 20, 1930, pp. 5–6, 118–120; Chem. Abs., vol. 24, 1930, p. 2365.

Equations and table of constants involved in calculations based on the reaction $CO+H_2O=H_2+CO_2+$ 10,400 cal.

———. *See* abs. 260, 261.

2479. Nitzschmann, R., and Lipka, H. [Volumetric and Equilibrium Relations of the Reaction $CH_4+H_2O\rightleftharpoons CO+3H_2$.] Metallbörse, vol. 19, 1929, p. 1014–1015; Chem. Abs., vol. 23, 1929, p. 3611.

Equations, tables, and illustrative problems.

Nobori, H. *See* abs. 1683, 1684, 1685, 1687, 1688, 1689, 1690, 1691, 1692, 1694.

Nobori, H., and Kawai, S. Manufacture of Fatty Acids by the Oxidation of Paraffin. XXIII. Oxidation of High-Melting Paraffins. *See* abs. 1696.

Noguchi, M. *See* abs. 1684, 1685, 1688.

2480. Noton, C. H. Synthetic Fuel From Peat. Ind. Chemist, vol. 17, 1941, pp. 304–306; British Chem. Abs., 1942, B, p. 70.

Peat is completely gasified in a Pintsch-Hillebrand plant to yield a synthesis gas with the proper ratio of $CO:H_2=1:2$ at a gas-making efficiency of over 69%. The necessary heat for operating the regenerator (95 B. t. u.) is supplied 45 B. t. u. by the waste gas from the Fischer-Tropsch plant and 50 B. t. u. by burning peat. The cost, with peat at RM7/ton, is RM 0.34 per 1,000 cu. ft. of synthesis gas.

2481. Novak, H. [Synthetic Production of Oils and Methyl Alcohol.] Chem. Obzor., vol. 1, 1926, pp. 48–51: Chem. Zentralb., 1927, II, p. 1319.

Processes of F. Fischer, G. Patart, and E. Audibert are described. It is pointed out that, at present prices, the use of MeOH in motors is not practical.

2482. Novikov, I. [Apparatus for High-Temperature Processes Under High Pressures.] Novosti Tekhniki, 1939, No. 30, pp. 36–37; Khim. Referat. Zhur., 1940, No. 6, p. 138; Chem. Abs., vol. 36, 1942, p. 4739.

Experimental plant of the Academy of Science of U. S. S. R. constructed an autoclave for syntheses (NH_3, MeOH, etc.), cracking, hydrogenation, etc. The autoclave consists of a reaction chamber within an electric oven. The pressures on both sides of the walls of the reactor are regulated by passing out the excess gases through valves in the reactor and the oven. With a 500-atm. outside pressure for the reactor, inner working pressures of 800, 1,000, and 1,200 atm., with corresponding working temperatures of 800° 700°, and 600°, respectively, are possible.

2483. Nowotny, H., and Juza, R. [Cobalt Reduced in Hydrogen.] Ztschr. anorg. Chem., vol. 253, 1945, pp. 109–112; Chem. Abs., vol. 43, 1949, p. 2883.

Possibility that in different preparations of Co by reduction, the Co may have the hexagonal structure or the hexagonal- or cubic-close packing has been confirmed on the basis of energy relationships.

2484. Noyes, A. A., and Smith, L. B. Dissociation Pressures of Iron Nitrides. Jour. Am. Chem. Soc., vol. 43, 1921, pp. 475–481; Chem. Abs., vol. 15, 1921, p. 1245.

Equilibrium conditions of the reaction between Fe, NH_3, solid Fe nitrides, and H_2 at 460° are determined. The equilibrium constant given by the expression $(p_{NH_3})^2/((p_{H_2})^3$ was found to vary with the proportion of N present in the solid phase. Thus with increasing N content this expression remained constant at the value 1.0 until the atomic ratio N : Fe became 1 : 9; later increased rapidly, namely, to 5.2 for N : Fe=1 : 7.7 and to 30 for N : Fe=1 : 4.9; and finally assumed the much smaller value 2.1 for N : Fe=1 : 2.6. These results indicate the formation: 1st, of a nitride of small N content, perhaps Fe_8N; then either of a metastable nitride, such as Fe_4N in solid solution with the 1st one, or of 2 separate metastable nitrides, such as Fe_8N and Fe_4N as separate solid phases; and, finally, of a stable nitride, probably the well known Fe_2N. By combining this equilibrium constant with the constant $(p\mathrm{HN}_3)^2/p_{N_2}(p_{H_2})^3$ for the formation of ammonia, the dissociation pressures $p\mathrm{N}_2$ of the nitrides in the various solid phases were computed to be 20,000, 102,000, 590,000, and 41,000 atm., respectively.

2485. Nury, G. Influence of the Disappearance of Antiferromagnetism of Nickel Oxide on the Chemical Activity of This Oxide. Compt. rend., vol. 234, 1952, pp. 946–948; Chem. Abs., vol. 46, 1952, p. 10723.

Amount of reduction of NiO in 2 hr. in H_2 at temperatures 200°–425° shows maximum at 265° and 350° and is essentially zero in the ranges 300°–340° and 355°–400°. The metallic Ni formed is estimated by a magnetic method. The 265° maximum may be related to the dilation anomaly in NiO. The general low rate in the 300°–400° range appears related to the loss of antiferromagnetism of NiO in this range. The sharp maximum at 350° appears related to the Curie point of Ni.

———. *See* abs. 1060, 1061.

Nussbaum, R., Jr., and Frolich, P. K. Catalysts for Formation of Alcohol From Carbon Monoxide and Hydrogen. VII. Studies of Reduction of Methanol Catalyst. *See* abs. 1103a.

2486. Oberdisse, K. [Utilization of Synthetic Fats in the Human and Animal Organism.] Ztschr. ges. exptl. Med., vol. 114, 1944, pp. 60–74; Chem. Abs., vol. 44, 1950, p. 2615.

Fatty acids, obtained in the Fischer-Tropsch synthesis, were nearly saturated and contained even and odd numbers of C atoms between C_{10} and C_{20}. In man an average of 6.5%, in dogs 7.9%, of a simple dose of fat was found in the feces; ⅔ of it was in the form of free fatty acids and soaps. The blood-fat level rose to a maximum in men and dogs 3 hr. after feeding. The blood ketone bodies increased 95 and 100% in men and dogs, respectively, the maximum being reached some time after the maximum fat value. The alkali reserve was not affected. The synthetic fats were as well tolerated as the natural ones.

2487. Oberfell, G. G. Utilization of Natural Gas in the United States. Oil Gas Jour., vol. 44, No. 32, 1945, pp. 76–78; Gas Age, vol. 96, No. 13, 1946, pp. 12–15, 50; vol. 97, No. 1, 1946, pp. 25–29, 58–60; Am. Gas Assoc. Monthly, vol. 28, No. 1, 1946, pp. 7–13, 48; Nat. Petrol. News, Tech. Sec., vol. 38, No. 1, 1946, R, pp. 46–51; Petrol. Refiner, vol. 25, No. 1, 1946, pp. 94–104; Petrol. Eng., vol. 17, No. 4, 1946, pp. 158, 160, 164, 166, 168, 170, 174, 176, 178; Min. and Met., vol. 27, 1946, pp. 165–172.

Paper read before the Chicago section of American Institute of Mining and Metallurgical Engineers. The competitive position of natural gas with respect to coal as a raw material for Fischer-Tropsch type processes in the United States will depend upon the relative economics, efficiencies of utilization, and over-all reserves of coal and natural gas available. It is generally agreed that gasoline from dry natural gas as a starting material is cheaper to produce than the same product from coal as the raw material. For example, with natural gas at $0.05 per 1,000 cu. ft., the cost per bbl. of gasoline produced (10,450 cu. ft. per bbl.) is approximately $0.52. To compare favorably with this, the price of coal per ton would need to be about $0.77 on the basis of 1,360 lb. of coal per bbl. of gasoline. On the other hand, the synthesis process using natural gas will not be able to compete with present refinery methods utilizing crude petroleum until the price of crude reaches about $1.75–$2.00 per bbl. The successful commercial development of the Fischer-Tropsch process should lead to its integration with the natural gasoline industry, with which it is complementary in that it affords an outlet for residual gas and for dry gas without a pipeline market and with the natural gas fuel industry with which it promises to compete. Furthermore, the process is of considerable economic importance to the chemical industry in its application to the synthesis of many chemical products.

2488. ———. Reserves of Natural Gas. Oil Gas Jour., vol. 47, No. 46, 1949, pp. 118, 122, 125, 126, 129, 133, 137.

As of January 1, 1949, the total proved reserves of natural gas in the United States amount to 174 trillion cu. ft. or about a 37-yr. supply based on consumption in 1948. It is expected that further exploration will add materially to this figure and that such additions, plus an everchanging competitive fuel picture, will result in adequate natural-gas supplies for many years to come. The uses and probable development along chemical lines are discussed, and the conversion to liquid fuels by the Fischer-Tropsch synthesis process is reviewed. It is not believed that the peak synthetic-gasoline production from natural gas will ever amount to more than a minor proportion of the total gasoline supply of the Nation, because of the many other profitable markets for natural gas.

2489. Oberfell, G. G., and Thomas, R. W. Picture for Liquefied Petroleum Gases. Oil Gas Jour., vol. 45, No. 5, 1946, pp. 60–61.

Condensed paper presented at the annual meeting of the Liquefied Petroleum Gas Association. A recent development that enters the liquefied-petroleum-gas picture is the so-called Fischer-Tropsch process, which uses natural gas as raw material for the production of heavier hydrocarbons. The production of gasoline and other products by this method may yield sizable quantities of C_4H_{10} and C_3H_8. Therefore, installations of this process for the production of petroleum products are not expected to diminish the overall supply of liquefied petroleum gases.

2490. Oberholtzer, J. E. Natural-Gas Industry of Alberta, Canada. Coke and Gas, vol. 11, 1949, pp. 55–58.

Alberta has large reserves of natural gas. The gas is approximately 90% CH_4 and has a heat value of about 1,000 B. t. u. per cu. ft. Available reserves are increasing faster than consumption. The production of synthetic gasoline by the Fischer-Tropsch process is worthy of serious consideration as related to the reserves of both coal and natural gas. The production of a wide range of chemicals and plastics is also a future possibility.

Oblad, A. G. *See* abs. 2285.

2491. Obolentsev, R. D. [Research on Isomerization of Liquid Normal Aliphatic Hydrocarbons.] Jour. Gen. Chem. (U. S. S. R.), vol. 16, 1946, pp. 77–93; U. O. P. Co. Survey Foreign Petroleum Literature Transl., 634, 1946.

As one of the starting materials, synthin, which consisted of a mixture of paraffins (63.5 wt. %), olefins (20.6%), and aromatics (15.9%), was used. The catalyst was a fused mixture of $AlCl_3$ with other salts. The synthin was first hydrogenated over Ni to a Br no. of 0–1 and the product freed from aromatics with fuming H_2SO_4 to a negative formolite test. The resulting mixture was fractionated and refractionated in laboratory distillation columns, yielding finally about

10 l. of concentrates containing normal hexane, heptane, and octane. Their content of branched chain hydrocarbons was within 8–12%. Many fractionations of these concentrates gave the normal paraffins desired in 94–97% concentration.

2492. Obryadchikov, S. N., and Marushkin, B. K. [Investigation of the Fluid Catalyst Process.] Neftyanoe Khoz., vol. 24, No. 11, 1946, pp. 36–45; Chem. Abs., vol. 41, 1947, p. 3946.

Laws relating to the behavior of finely divided solid particles in conditions simulating the fluid catalyst process were studied on models made of glass, by using fine sand suspended in a stream of water. Data obtained on the particle concentration (in gm./cc.) and the height of the fluidized layer of sand of different sizes, at various water-feed rates, are given in graphs. It is shown that the pressure losses are directly proportional to the weight of the particules in the fluidized layer. In a system with continuous circulation of the catalyst from the bottom towards the top, the concentration of the catalyst at various levels of the reactor can be determined by measuring the pressure gradient at the different levels or, conversely, with uniform concentration of the flowing catalyst in the cylindrical portion of the reactor, the pressure loss is proportional to the height of the layer.

2493. O'Connor, B. Silica-Gel Percolation. Ind. Eng. Chem., vol. 40, 1948, pp. 2102–2103; Chem. Abs., vol. 43, 1949, p. 1169.

Discusses use of silica-gel percolation in studying the types of compounds present in the products of the Fischer-Tropsch synthesis. The compounds of similar boiling point are separated according to their adsorption affinity with silica gel, which increases in the order of paraffins, olefins, aromatics, and oxygenated compounds. The differentiation of the 2 latter compounds is improved by using an azo dye.

Ode, W. H. *See* abs. 3159.

2494. Odell, W. W. Commercial Possibilities in the Use of Synthetic Hydrocarbon Processes in the Gas Industry. Bureau of Mines Rept. of Investigations 2903, 1928, 15 pp.; Fuel, vol. 8, 1929, pp. 178–187; Chem. Abs., vol. 23, 1929, p. 1245.

Peak requirements demand available gas-generating apparatus, which is idle a large part of the year. To care for irregular demand, as well as to insure independence of petroleum products for enriching, it has been suggested that water-gas and synthetic hydrocarbon production be carried out together to give an enriched gas. During off-peak demand, liquid hydrocarbons could be prepared for motor fuels and for enriching requirements of future peak gas production. Enough data are not available to determine the applicability of this process; purification requirements are uncertain, and the commercial development of the proper type of catalyst has not been studied.

2495. ———. Possibilities in Synthetic Hydrocarbon Processes. Gas Age-Record, vol. 63, 1928, pp. 37–41, 48–50; Chem. Zentralb., 1930, I, p. 1409; Chem. Abs., vol. 23, 1929, p. 4553.

Discusses commercial and economic possibilities of making hydrocarbons synthetically from water gas in some detail. Gives tables of yields and costs.

2496. ———. Re-Forming Natural Gas in Water-Gas Generators, With Substantially Complete Elimination of Entrained Carbon. Bureau of Mines Rept. of Investigations 2973, 1929, 10 pp.; Chem. Abs., vol. 24, 1930, p. 710.

When steam and a hydrocarbon gas are admitted to the incandescent fuel bed of a standard water-gas generator, a re-formed gas is produced, which is comprised chiefly of H_2, CO, and CH_4. When the amount of steam is too low, C resulting from the cracking of the hydrocarbons is entrained in the gas. A higher temperature is required to crack CH_4 than the higher hydrocarbons. The composition of the re-formed gas can be controlled, and the specific gravity and heating value can be adjusted as necessary. Increased air blasting (increased temperatures) decreases CH_4 content and increases H_2. The low limit is about 10% CH_4 and 60% H_2, giving a gas of 350 B. t. u. heating value. Relative amounts of steam and hydrocarbon influence the H_2:CO ratio. The low limit is substantially the same as that for water gas, 1.2:1; the upper limit without entrained C is about 3:1. Less heat is required for the generation of a unit vol. of reformed gas than straight water gas; hence less generator fuel is used. Gasmaking capacity is increased materially by a blow run. Gives operating data.

2497. ———. Re-Forming Natural Gas. Bureau of Mines Tech. Paper 483, 1930, 54 pp.; Chem. Abs., vol. 25, 1931, p. 1058.

When the ignited fuel bed of a water-gas generator is blasted alternately with air and both steam and natural gas in controlled proportions, re-formed gas is produced substantially without entrained C, the gas consisting of CO, H_2, and lesser CH_4. The thermal efficiency and gasmaking capacity are higher in generating re-formed gas in this manner than in making water gas, and the fuel used per 1,000 cu. ft. of re-formed gas is lower. Gives operating data and factors influencing results.

2498. ———. Gasification of Solid Fuels in Germany by the Lurgi, Winkler, and Leuna Slagging-Type Gas-Producer Processes. Bureau of Mines Inf. Circ. 7415, 1947, 46 pp.; PB 97,778.

Each of the 3 processes uses O_2 and steam, and the Winkler fluidized and the Lurgi pressure processes use finely divided, highly reactive fuel, whereas the slagging-type process uses sized furnace coke. It is believed that the Winkler process as now developed and the Lurgi process with some improvement or in a modified form may be used effectively under certain conditions and with particular fuels in the United States. This is especially true with low-cost fuel and O_2. Operating data relative to the 3 processes are presented in tabulated and summarized form. Some analysis of O_2 cost is given, and some data on the manufacture of city gas in conjunction with the production of synthetic liquid hydrocarbons are appended.

Oelsen, W. *See* abs. 1965.

2499. Oel und Kohle. French Efforts at Self-Sufficiency in the Provision of Motor Fuels. Vol. 14, 1938, pp. 587–588.

Production of liquid fuel by coal hydrogenation and the Fischer-Tropsch processes and the use of gas producers using charcoal on vehicles.

2500. Offenberg, W. [Gasification of Solid Fuels With Oxygen Under Pressure.] Stahl u. Eisen, vol. 63, 1943, pp. 936–939; British Abs., 1946, B, I, p. 123.

Solid, noncaking fuel (brown coal, lean bituminous coal, gas coke) in a 2–25 mm. size is gasified in a refractory-lined, water-jacketed reaction vessel by a mixture of superheated steam and O_2 at 20–30 atm. The gas after cooling is washed with oil and then with H_2O, which removes most of the CO_2 and H_2S. Residual H_2S is removed by Fe_2O_3, and the purified gas is delivered at 20–25 atm. to high-pressure mains. The gas has a gross calorific value of 4,000–4,500 kcal. per m.^{3}, depending on the reactivity of the solid fuel. That from a brown coal contained CO_2, 3.0; C_nH_m, 0.5; O_2, 0.1; CO, 22.8; H_2, 48.7; CH_4, 22.6; N_2, etc., 2.3%; the total S was 0.1 gm. per 100 m.^{3}, and NO was 0.052 cc. per m.^{3} The consumption of O_2 is approximately 0.18 m.^{3} and that of steam 1.25 kg. per m.^{3} of purified gas. Production cost is competitive with that of other gasification processes.

Ogarkov, N. P. *See* abs. 2754.

2500a. Ogawa, E., and Murata, K. Catalytic Action of Nickel-Iron-Cobalt Wire Under Tension on the Reaction Between Ethylene and Hydrogen. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, pp. 386–387 (in English); Chem. Abs., vol. 44, 1950, p. 7,636.

Activation energy of the $H_2+C_2H_4$ reaction is raised from 16,400 to 17,800 cal. by placing under tension Ni–Fe–Co alloy wire used as a catalyst. The difference is caused by the orientation of the magnetic axis of each magnetic domain from its random distribution.

2501. Ogawa, E., Tada, M., and Okuna, T. Studies of Catalytic Action by Conversion Between Para-Hydrogen and Ortho-Hydrogen. I. (a) Conversion by Magnetized Nickel Wire. (b) Conversion by Catalyst for Ammonia Synthesis. Jour. Soc. Chem. Ind. (Japan), vol. 45, suppl. binding, 1942, pp. 387–389; Chem. Abs., vol. 44, 1950, p. 7637.

At 73°, the activation energy of the *o*–*p*–H_2 conversion over Ni was 3,000 cal. for unmagnetized catalyst and 6,000 for magnetized catalyst. At 112° the effect of magnetization disappeared, indicating that the conversion changes from a magnetic to activated adsorption mechanism. The same change of mechanism exists in NH_3 synthesis.

Ogawa, S. *See* abs. 2299.

Ogawa, T. *See* abs. 1754a, 3176.

Ogawa, T., Kimumaki, J., and Fujisaki, T. Iron Catalyst for Synthetic Petroleum. II. Some Characteristic Properties of Iron Catalyst for Synthetic Petroleum. *See* abs. 3177.

2502. Ogawa, T., Matui, A., and Senoo, H. Oxidation of Methane. I. Reaction Between Methane and Ferric Oxide. Jour. Soc. Chem. Ind. (Japan), vol. 41 1938, suppl. pp. 399–400; Chem. Abs., vol. 33, 1939, p. 3327.

Gases produced by the reaction at 900°, 1,000°, and 1,100° of 200 gm. powdered Fe_2O_3 in a porcelain tube, 2.6 cm. in diameter, heated by an electric furnace and CH_4 introduced at the rate of 2 l. per hr. were analyzed at intervals for CH_4, CO, CO_2, and H_2, and the results were plotted. At first the reaction yielded CO_2 and H_2O, then chiefly CO and H_2 at a constant ratio of approximately 1:2 for several hr., and finally the concentration of H_2 increased owing to the reaction $CH_4=C+2H_2$. At 1,100° after 2.5 hr., the product consisted of about 21% CO and 40% H_2. The catalyst was regenerated with a limited amount of atmospheric O_2 in a separate vessel. Conclusion: The catalyst is suitable for the synthesis of $(CO+2H_2)$.

2503. ———. Oxidation of Methane. II. Reaction Between Methane and Bog Iron Ore. Jour. Soc. Chem. Ind., (Japan), vol. 41, 1938, suppl., p. 400; Chem. Abs., vol. 33, 1939, p. 3327.

Bog iron ore (I) (61.5% Fe_2O_3, 21.1% SiO_2, and 2.9% MnO_2) and regenerated (I) were substituted for the Fe_2O_3 in the tests made at 1,100°. At the end of 2.5 hr., about 20% CO and 45% H_2 were present in the products when (I) was used. When a 200-gm. portion of (I) was completely reduced to metallic Fe (+impurities) and regenerated with a limited amount of O_2 (4.2–4.5 liters), less than 5% each of CH_4 and CO_2 was produced from the start, and the production of CO and H_2 was fairly constant at 22–24% CO and 58–60% H_2.

2504. Ogawa, T., Matui, A., Nagai, H., and Hidetaka, S. Oxidation of Methane. III. Experiment on the Apparatus Heated by Internal Combustion. Jour. Soc. Chem. Ind. (Japan), vol. 43, 1940. suppl., pp. 116–117; Chem. Abs., vol. 34, 1940, p. 5627.

Mixtures containing CO and H_2 in ratio of approximately 1:2 were prepared by alternately passing, at a rate of 3 m.^{3} per hr., CH_4–air mixtures, which burn to produce a temperature of 1,380°, and CH_4, which absorbs heat on cracking and lowers the temperature to 1,220°, through a Ni–Cr alloy tube containing a Ni catalyst (exact composition not given) and ignited Fe balls made of equal amounts of Fe_2O_3 and MgO. The exit gas from a typical run had the following composition: CO_2, 3.5; O_2, 0.9; CO, 21.8; H_2, 56.5; CH_4, 16.3; and N_2, 1.0%. The mount of conversion was increased by putting Ni–kaolin balls above the Fe balls in the tube. In a typical run with this latter arrangement, the exit gas contained CO_2, 8.7; O_2, 0.9; CO, 27.4; H_2, 56.7; CH_4, 3.6; and N_2, 2.7%. Gives diagram of the apparatus and tabulates results. It is stated that the process could be used industrially.

Ogden, G. *See* abs. 3341.

2504a. Ogura, T. Decomposition of Methane by Oxidation. Bull. Chem. Soc. Japan. vol. 16, 1941, pp. 303–324, 356–367; Chem. Abs., vol. 41, 1947, p. 4,435.

Reaction between CH_4 and steam was carried out in the presence of a Ni catalyst under various conditions. The influence of amount of steam, temperature, and pressure of the reaction mixture on the decomposition rate of CH_4 were studied. The decomposition of CH_4 containing O_2, CO_2, or CO was carried out in the presence of oxides of metals, Ni, Co, Cu, Fe, and Cr. The influences of amount of mixing gases, reaction temperature, and pressure on the decomposition rate of CH_4 were studied.

2505. ———. [Oxidative Decomposition of Methane.] Bull. Chem. Soc. Japan, vol. 16, 1941, pp. 262–273 (in German); Chem. Abs., vol. 36, 1942, p. 3777.

55 references are listed for the oxidation or partial oxidation of CH_4 to (1) H_2O, CO_2, or CO; (2) H_2, CO_2, or CO; and (3) MeOH, CH_2O, HCO_2H, AcOH, acetone, and other substances. Equilibrium data were calculated for the reaction of CH_4 with (1) steam, (2) O_2, and (3) CO_2.

———. *See* abs. 1651.

2506. Ogura, T., and Huzimura, T. Reaction Between Methane and Steam. Jour. Chem. Soc. Japan, vol. 60, 1939, pp. 139–148; Chem. Abs., vol. 34, 1940, p. 2569.

Reaction $CH_4+2H_2O=CO_2+4H_2-38.5$ cal. was studied with natural gas containing CH_4, 95.2; C_2H_6, 1.9; CO_2, 1.6; C_nH_m, 0.3; air, 1.0%. For this reaction a catalyst is necessary. With an effective catalyst the reaction is completed at 550°–600°. $H_2O:CH_4=7:10$ is the best ratio. Ni is the best catalyst: However, if it is used alone its catalytic activity decreases at higher temperature, 700°, owing to its melting. Addition of a promotor prevents this inactivation. With Al_2O_3 as promotor, $Ni:Al_2O_3=1:0.025$ in mols. gives the greatest activity. Addition of a minute amount of alkali does not affect the catalytic activity but decreases the durability of the catalyst. Concentration of the catalyst 10%, particle size 3–4 mm., contact period of 25–30 sec. are recommended. Temperatures below 700° for the roasting and below 300° for the reduction give the best catalyst. A Ni–Al_2O_3–kaolin catalyst prepared according to these observations gave good results in an experiment lasting 150 hr.

2507. Ogura, T., and Ichimaru, T. Reaction of Methane and Oxygen. Jour. Soc. Chem. Ind. (Japan), vol. 47, 1944, pp. 540–543; Chem. Abs., vol. 42, 1948, p. 6082.

For the purpose of obtaining a mixture of CO and H_2, CH_4 was oxidized under various conditions. When no catalyst was used, CH_4 and O_2 did not react below 600°. As catalyst, Co was the most effective and Ni was the next. With Co as catalyst, the reaction takes place even below 300° when more than 2 times the volume of O_2 is added to CH_4, producing CO_2 and H_2O. When an equivalent amount of CH_4 and O_2 is taken, CO_2 and H_2O are produced, and a part of the CH_4

remains below 800°, while above 800°, all CH_4 is changed to CO and H_2. Admixture of N_2 retards the reaction, and admixture of H_2O promotes it. When mixtures of CH_4 and O_2 were exploded, the product was variously CO_2, CO, H_2O, and H_2, according to the ratio at which CH_4 and O_2 were taken. A semi-industrial experiment showed that preparation of a mixture of CO and H_2 by suitably oxidizing natural gas is successful.

2508. Ogura, T., and Nagai, H. Reaction Between Methane and Carbon Dioxide. Jour. Soc. Chem. Ind. (Japan), vol. 45, 1942, pp. 170–173; Chem. Abs., vol. 43, 1949, p. 1944.

Reaction of CH_4 and CO_2 in various proportions at 500°–1,200° under ordinary pressure in the presence of Co or Ni catalysts was studied on experimental and semi-industrial scales for the purpose of finding the best conditions for obtaining good yields of CO and H_2 with natural gas and some industrial waste gases as raw materials. The reaction was accelerated by using good catalysts and by raising the temperature. When there was not enough CO_2, deposition of C was noticed. This was prevented by adding steam to the mixed gas.

2509. Öhman, E. Crystal Structure of Martensite. Nature, vol. 127, 1931, pp. 270–272; Chem. Abs., vol. 25, 1931, p. 2400.

Present knowledge of tetragonal martensite is summarized, and results of earlier investigators are reviewed with reference to C content and lattice dimensions. The author employed Cr–K–radiation and obtained photograms of quenched steel specimens in which the line (101) of the tetragonal phase is separated from the γ–Fe line (111). Thus, it was possible to determine the lattice dimensions of the tetragonal structure. Results agree with those of Kurdumoff and Kaminsky that the tetragonal martensite is a supersaturated solution of C in α–Fe. Ferrite and tetragonal martensite are thus one and the same phase, but, as they are often present in one and the same specimen as separate constitutents, it seems convenient to denote the tetragonal phase as α′. Westgren and Phragmen suggested that the C atoms dissolved in γ–Fe do not occupy any points of the face-centered lattice but are statistically distributed in the interstices between the Fe atoms. Seljakow, Kurdumoff, and Goodtzow suggested that the same might be the case in the α′–phase but the author thinks this improbable as the space available for the C atoms would be extremely small. Another probable explanation is that there is a complex substitution in such a way that a group of 2 C atoms is substituted for 1 Fe atom in the lattice. These compounds have a tetragonal structure in which the C_2 group is oriented parallel to the tetragonal axis, an explanation that holds equally well for tetragonal martensite. By density measurements, it is shown that the assumption of a complex substitution of C atoms is in good agreement with X-ray intensities. The only suggested structure of tetragonal martensite that explains the observed density, the increase of volume with the C content, and the elongation of 1 of the crystallographic axes may be described as follows: In the body-centered lattice groups of 2 C atoms statically distributed replace some of the Fe atoms. The C atoms are most probably oriented in such a way that the axes of the C_2 groups parallel the tetragonal axis of the lattice.

2510. ———. X-Ray Investigation on the Crystal Structure of Hardened Steel. Jour. Iron Steel Inst. (London), vol. 123, 1931, p. 445; Chem. Abs., vol. 25, 1931, p. 4502.

X-ray study of quenched steels confirmed the existence of the tetragonal phase, the axial ratio of which increased with increasing C content. From a consideration of these data it is concluded that martensite consists of a solid solution of C in body-centered Fe. On effective quenching, the tetragonal phase has the same composition as the parent austenite, as proved by the direct relationship between C content and space-lattice dimensions. It appears probable that the C atoms disolved in α-Fe form a complex substitutional group in which 2 C atoms replace 1 Fe atom. On tempering, the tetragonal phase decomposes continuously with a progressive decrease in axial ratio. The causes of the hardness of martensite are discussed. 47 refs.

2511. ———. [Carbides in the Iron–Manganese–Carbon System.] Jernkontorets Ann., vol. 128, 1944, pp. 13–16; Chem. Abs., vol. 39, 1945, p. 3198.

X-ray study made in 1926 of the carbides *present* in the above system revealed a hitherto unknown double carbide of Mn and Fe, which has a monoclinic crystal structure. By solution of C in molten Mn, carbides are produced, which, according to X-ray powder photographs, are isomorphous with the Cr carbides $Cr_{23}C_6$ and Cr_7C_3. As the powder photographs are in exact agreement with those obtained for the above Cr carbides, the Mn carbides probably have the formula $Mn_{23}C_6$ and Mn_7C_3. The latter has been observed only in alloys with more than 80% Mn, whereas $Mn_{23}C_6$ is found with up to 50% Fe and less than 6% C present. With more than 50% Fe cementite is the only carbide formed. Both cementite and $Mn_{23}C_6$ are present even when the Mn content is up to 70%. Mn can replace Fe in cementite to a considerable extent.

2512. Ohme, W. [Neutralization of Fatty Acids Formed in Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen.] Oel u. Kohle Erdoel Teer, vol. 38, 1942, pp. 465–467; Chem. Abs., vol. 37, 1943, p. 5569.

Acids cannot be completely neutralized by aqueous $NaHCO_3$ unless they are in contact with the latter for very long periods. The aqueous Na_2CO_3 used in practice for neutralization is converted, to a large extent, into $NaHCO_3$ at the prevailing temperature and pressure owing to the high CO_2 content of the synthesis end gases. When the CO_2 content of the latter is high, special neutralization processes are necessary.

2513. ———. Conversion of Fat Acids From the Fischer-Tropsch Synthesis to Ketones. Oel u. Kohle Erdoel Teer, vol. 40, 1944, pp. 87–89; Ind. Chemist, vol. 21, 1945, pp. 270–274; Chem. Abs., vol. 39, 1945, p. 277.

Fat acids formed as byproducts in the Fischer-Tropsch synthesis were obtained by extracting certain hydrocarbon fractions with caustic and acidifying the solution. Part of the fat acids was distilled at 0.5 mm. Hg and another part was directly converted into the Ca salts by reaction with an excess of lime. The Ca salts were subjected to dry distillation at 350°–650°, and the ketones formed were distilled at atmospheric pressure and redistilled under vacuum. The bulk of the ketones boiled 240°–300°, and the melting point varied from −10° to +30°; it is assumed that mixed ketones with 12–17 C atoms have been formed. The fractions obtained by distillation of the original fat acids represent C_5, C_8, C_{10}, C_{11}, C_{12}, C_{15}, and C_{18} fat acids. Each fraction was individually converted into the corresponding ketones at temperatures ranging 280°–600°, and the average yield amounted to 70–80%. The ketones were not uniform, as indicated by their rather wide boiling range (50°–70°). The melting point of the ketones increases with the number of C atoms from −50° to −62° for C_5 ketones, over −10° to +20° for the C_{11} ketones, and to 32°–44° for the C_{15} ketones. The ketones are partly liquids of agreeable odor and partly waxlike substances; they might find use as plasticizers and in the perfume industry.

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2514. Ohtsuka, H., and Tomita, N. Analysis of Synthetic Gasoline Obtained by Fischer Process. Jour. Soc. Chem. Ind. (Japan), vol. 44, 1941, pp. 746–747; Chem. Abs., vol. 42, 1948, p. 2080.

If the material is found by hydrogenation to contain no aromatic hydrocarbons, the following short procedure of the analysis gives a result accurate enough. Fractionate the sample into 4 portions: (A) boiling up to 65°, (B) 65°–105°, (C) 105°–140°, (D) 140° to dry point. Wash each fraction with 2 vol. 87% H_2SO_4, and in fractions (A) and (B) consider the loss as unsaturated hydrocarbons and the remainder as saturated. In fractions (C) and (D), wash the remaining portion with 3 vol. 99% H_2SO_4, and consider the final remainder as saturated hydrocarbons, and the balance as unsaturated.

2515. Oil and Gas Journal. Chicago Corporation to Build Carthage Field Plant. Vol. 43, No. 39, February 3, 1945, p. 79.

Chicago Corp., Corpus Christi, will construct a cycling plant in the Carthage gas field, East Texas, capable of processing 150,000,000 cu. ft./day. Preliminary plans have been discussed with PAW officials for installing a Fischer-Tropsch plant, which would mark the 1st commercial installation of this type for synthetic production of liquid petroleum products from natural gas.

2516. ———. Fischer-Tropsch Hydrocarbon Synthesis. Vol. 43, No. 47, 1945, p. 214.

This process involves the catalytic conversion of water gas or natural gas into hydrocarbons. Synthesis gas is obtained thus:

$$(1)\ C+H_2O=CO+H_2,$$

$$(2)\ CH_4+H_2O=CO+3H_2.$$

If the latter mixture is reacted in this proportion, the tendency is to form CH_4 and lower molecular weight hydrocarbons. Lower % of H_2 and higher temperatures form mainly CH_4, especially with Ni as catalyst. Fe catalysts show the best results in synthesizing high-octane number products; it produces more isoparaffinic and olefinic products than do either Co or Ni; a sintered Fe catalyst is reported as the most efficient so far developed in this country. The mixture of charge gases for reaction with Fe catalysts should be richer in CO, probably more nearly a 1:1 ratio. Ni catalyst tends to form highly saturated, low molecular-weight hydrocarbons; Co also produces saturated hydrocarbons but generally of higher molecular weight!; Ru produces paraffins of extremely high molecular weight up to 23,000. Lubricating oils are made by polymerizing olefins formed in the synthesis with Fe or other olefin-forming catalyst, as with $AlCl_3$. Flow sheet.

2517. ———. High-Octane Motor Fuel From Natural Gas. Vol. 43, No. 36, 1945, pp. 48–49.

Development is announced of the Fischer-Tropsch process, which makes possible the production of gasoline from natural gas with a yield of 80% and an octane No. of 75 motor (83 research) for about $0.05 per gal., based on natural gas at $0.05 per 1,000 ft.^{3} and a plant depreciation of 10%. The new method is said to overcome successfully the problem of heat dissipation and accurate temperature control. Prewar European yields by the then existing methods were 30–40% of approximately 25 octane No. gasoline. The Kellogg Co. is prepared to build hydrocarbon synthesis plants using the process. Recently sintered Fe catalysts have been introduced, resulting in a product of a mixture of varying molecular weight hydrocarbons in which isoparaffins and even naphthenic and aromatic mixtures are the main constituents instead of the predominant normal paraffins formed with the Co and Ni catalysts.

2518. ———. Alberta Company Plans Gas-Synthesis Plant. Vol. 45, No. 5, 1946, p. 62.

Calgary Oil Co. is reported to be erecting a $100,000 pilot plant for making gasoline from natural gas, using a process said to be entirely original with the developing company. The plant will have a capacity of 2,000,000 cu. ft. gas per day, producing about 5 gal. of gasoline per 1,000 cu. ft. It is expected to be in operation by fall according to the United States Bureau of Foreign and Domestic Commerce.

2519. ———. Natural-Gas Investigation by the Federal Power Commission, Washington. Vol. 45, No. 8, 1946, pp. 60–61.

Abstract of testimony by P. C. Keith, president of Hydrocarbon Research, Inc., on the development of processes for making gasoline from natural gas and for gasifying and liquefying coal. (*See* abs. 1718.) Fuel reserves as of January 1, 1946, if converted into crude oil, would make a total of 6,326 billion bbl., divided; 21 billion bbl. from crude, 25 billion bbl. from natural gas, and 6,280 billion bbl. from coal synthesis. It is predicted that commercial production of gasoline from natural gas and from coal will take place within 5 yr. Experiments had been made in the production of city gas from coal, and a gas had been obtained of 600–900 B. t. u. at a cost of $0.17 per 1,000 cu. ft. It is estimated that gas could be produced at West Virginia coal mines and transported to New York for $0.242 per 1,000 cu. ft. By this process, 10,000 tons of coal would produce about 200,000,000 cu. ft. of gas. It is also stated that gasoline can be made from coal for $0.06 per gal., assuming the cost of coal at $2.00 per ton. The time will probably come in the not-too-distant future when this price will be competitive with petroleum and natural gas.

2520. ———. Stanolind Synthol Plant Now in Engineering Stage. Vol. 45, No. 37, 1947, p. 97; Petrol. Eng., vol. 18, No. 4, 1947, p. 24; Chem. and Eng. News, vol. 25, 1947, p. 240; Petrol Refiner, vol. 26, No. 2, 1947, pp. 168–169.

Stanolind Oil & Gas Co. reports that engineering work is now under way on the proposed commercial-scale Synthol plant to be built in the Hugoton gas field in Southwestern Kansas. It is expected to obtain a yield of 2.52 gal. of high-quality gasoline and 0.42 gal. of distillate fuels from each 1,000 cu. ft. of natural gas processed. The plant is being designed to process about 100,000,000 cu. ft. per day of low-heating-value gas currently unsuitable for sale as fuel. In the proposed process, feed gas is burned under a pressure of 300 p. s. i. with relatively pure O_2 to yield synthesis gas of closely controlled composition. A yield is estimated of 1 bbl. of crude synthetic oil and substantial amounts of oxygenated compounds from each 15,000 cu. ft. of gas charged to the plant. The synthesis is carried out under pressure in large fluid type reactors utilizing a special powdered–Fe catalyst.

2521. ———. Stanolind's Synthol Plant to be in Operation in 1949. Vol. 46, No. 2, 1947, p. 54.

According to J. H. Forrester, manager of manufacturing for Stanolind, the proposed synthol plant of Stanolind Oil & Gas Co., Kans., will be producing gasoline from natural gas on a commercial scale in 1949. The new plant will produce 5,300 bbl. of gasoline, 800 of fuel oil, and 1,060 of light hydrocarbons, and about 500,000 lb. of chemicals per day. J. E. Latta of the Tulsa laboratories said that the oxygenated compounds formed as byproducts will be useful in various fields as solvents, antifreeze preparations, and raw materials for the manufacture of fine chemicals. Included are alcohols, ketones, organic acids, and aldehydes.

2522. ———. Survey of Sites for Synthetic Fuels Plants. Vol. 47, No. 9, 1948, pp. 42–43.